

2 45 0382 9163



LANE MEDICAL LIBRARY STANFORD



LANE

MEDICAL



LIBRARY

Gift of Dr. E. B. Du Bois.

car

4. 11. 1930 - 1/2

HANDBOOK
OF
CHEMISTRY,
THEORETICAL, PRACTICAL, AND TECHNICAL.

BY
F. A. ABEL,
PROFESSOR OF CHEMISTRY AT THE ROYAL MILITARY ACADEMY, WOOLWICH; AND
ASSISTANT-TEACHER OF CHEMISTRY AT ST. BARTHOLOMEW'S HOSPITAL;
AND
C. L. BLOXAM,
FORMERLY FIRST ASSISTANT TO THE ROYAL COLLEGE OF CHEMISTRY.

WITH
A PREFACE BY DR. HOFMANN:
AND
NUMEROUS ILLUSTRATIONS ON WOOD.



PHILADELPHIA:
BLANCHARD AND LEA.
1854.

YSA981 3BA1

PHILADELPHIA:
T. K. AND F. G. COLLINS, PRINTERS.

C 30 H
A 141
1854

AMERICAN PUBLISHERS' NOTICE.

THE passage of this volume through the press has been carefully superintended by a competent editor, to secure the typographical accuracy so necessary to a work of this nature. The very thorough manner in which the authors have carried out their intention in its preparation, and the recent date of their labors, have rendered unnecessary any additions to the text. A number of wood-cuts have, however, been introduced, the entire absence of illustrations in the English edition appearing to be a drawback to the utility of the work as a guide to the student engaged in chemical operations, a purpose for which it is especially designed, and will be found eminently fitted.

PHILADELPHIA, *May*, 1854.

30218



PREFACE BY DR. HOFMANN, F. R. S.

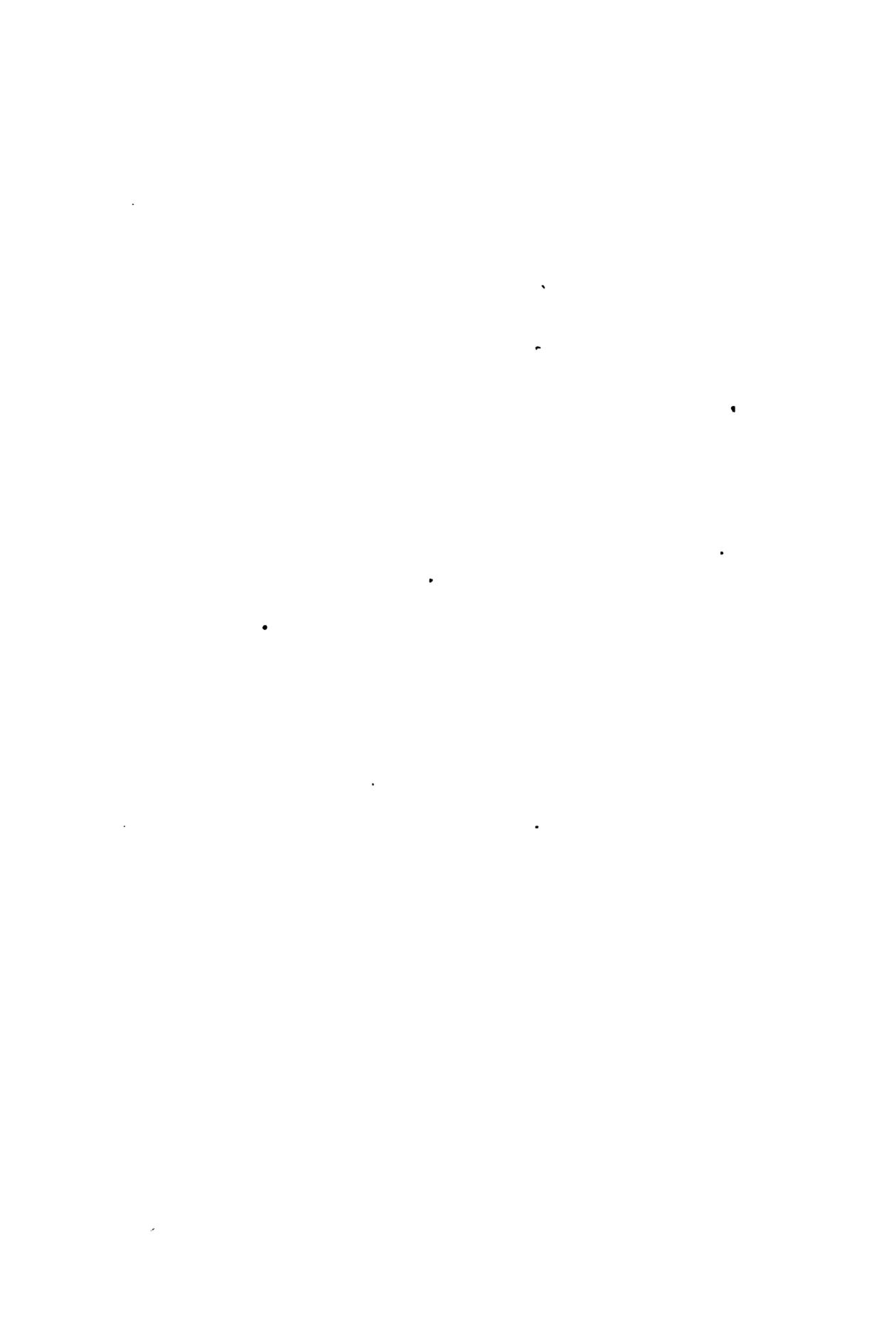
I FEEL much pleasure in complying with the wish expressed by Messrs. Abel and Bloxam, that I should introduce the present volume with a few prefatory remarks.

The Authors, after having received their chemical education in my laboratory, officiated for some years as my assistants, and I have had ample opportunities of witnessing their talents for imparting information, and smoothing the path of the Student, in every department of analysis. The present volume is a synopsis of their experience in laboratory teaching; it gives the necessary instruction in chemical manipulation, a concise account of general chemistry, as far as it is involved in the operations of the laboratory, and lastly, qualitative and quantitative analysis. The plan adopted in the instructions for analysis is *essentially* that which was first introduced by Baron Liebig, and which, modified in accordance with the progress of science, and with the special requirements of the English student, I have daily practised myself, for the last eight years, in this laboratory.

I have no doubt that the work of Messrs. Abel and Bloxam will fulfil the purpose for which it was written, and will prove a useful laboratory guide to the chemical student.

A. W. H.

ROYAL COLLEGE OF CHEMISTRY,
October, 1853.



P R E F A C E .

It is with considerable diffidence that the authors venture to bring this handbook before the public, at a time when the rapid growth of the science of which it treats has called forth numerous works on all its branches, from the pens of chemists of the highest eminence, which leave nothing to be desired in clearness of explanation or minuteness of detail. Although, however, the different departments of chemistry, theoretical, practical, technical, and analytical, have been made the subjects of separate treatises, which may well rank as the classics of the science, there is as yet no single work which presents, even to those who can devote but a comparatively short period to the study of this necessary branch of an extended education, such a general view of practical chemistry, in its several relations, as shall enable them to acquire, with the least possible expenditure of time, a knowledge which will either suffice for the ordinary applications of chemistry to the useful arts, or will serve as a sound basis for the education of a professional chemist. To attain this very desirable end, it is obviously necessary to furnish the student, in many cases, with the *result* only of a long chain of reasoning, which he would otherwise have to elaborate for himself, without any advantage to compensate for the sacrifice of time.

It was not the intention of the authors, even if it had been in their power, to write a complete system of chemical philosophy, but rather to content themselves with entering only so far into theoretical considerations as is absolutely essential in practice, and to bring the laws which determine the results of chemical operations before the student, in such a form, that their mutual dependence might be clearly perceived, and that they might readily fix themselves in the memory. In carrying out this design, however, some pains have been taken to avoid giving a concise description at the expense of a clear and satisfactory explanation.

The authors, having been engaged in laboratories where reference

has been made to them by chemical students respecting all the trivial difficulties met with in practice, have endeavored to turn their experience to advantage, in supplying information upon those points which, though apparently trifling, form great obstacles in the path of the beginner, and are not generally explained in treatises on scientific chemistry, since they are far too unimportant in themselves to occupy pages which are better filled with the philosophy of the science.

In the sections devoted to chemical manipulation, the various operations are described, as far as possible, in the order in which they would occur in the laboratory; thus, in considering the preparation of gases, attention is first directed to the construction of the apparatus, the bending of tubes, perforation of corks, &c.; next, the arrangements for collecting gases are noticed; and lastly, the transference of gases, and the various operations which may have to be performed upon them.

Chemical equations, which afford, at a glance, such clear explanations of various processes, have been freely used throughout that portion of the work which treats of elementary chemistry.

In describing the preparation of substances, details respecting the necessary apparatus have been omitted, since they have been given in the sections on manipulation. Since this book is not intended for a complete work of reference, or for an account of all the researches which have been made upon the subjects of which it treats, only those compounds are described, which appear to possess a certain practical importance. The descriptions of the processes involved in the different arts and manufactures have been stripped, to a great extent, of their mechanical details, in order that their chemical principles may be more readily mastered by the student. In the history of the chemical products obtained on a large scale, the methods employed by the practical chemist for ascertaining their value and for detecting the impurities to which they are liable, have, in most cases, been given.

There is appended to the technical history of the most important metals, a list of their chief minerals and ores, together with a brief outline of the methods usually followed in assaying the ores; these latter have been given more with the view of imparting to the student a general idea of such operations, than of enabling him to carry out, by the scanty directions there supplied, operations which fall strictly within the province of the metallurgist.

The reactions by which the rarer metals may be distinguished are introduced into their general history, to avoid unnecessary complication of the systematic course of analysis. When these metals are

supposed to exist in any substance under examination, special methods are always followed for their detection.

Some care has been taken, by diligent comparison with the latest monographs, to render the history of elementary chemistry a faithful representation, as far as the extent of the work will allow, of the present state of the science.

In the portion relating to analytical chemistry, a special description of the apparatus and operations of qualitative and quantitative analysis has been given. The authors have here made it their chief aim to be as concise as possible, omitting everything which has no direct bearing upon the systematic course, in order that the student may not be discouraged by a superfluity of detail, at the commencement of a study requiring so considerable an amount of patience.

Again, in constructing the systematic course, all unnecessary innovation has been avoided, the older methods of separation having been retained, except in cases where they yielded unsatisfactory results, when they have been replaced by others which have been submitted to the test of experiment; however, in the present progressive state of analysis, many of the methods are necessarily very imperfect; indeed, analytical tables must ever be regarded as provisional, and will constantly be liable to be superseded by others which are less circuitous or more accurate.

Under the impression that the student is far more likely to retain in his memory the various methods of quantitative separation of substances, when introduced in the form of practical examples, than when merely described in a general manner, a number of analyses for practice have been selected, in which the most important separations are effected.

We have derived no small gratification from the circumstance that this work has received the approbation of our friend and former teacher, Dr. Hofmann.

LONDON, *October*, 1858.

CONTENTS.

INTRODUCTION.

SPECIFIC GRAVITY—Determination of the specific gravities of solids, liquids, gases, and vapors—Corrections for temperature and pressure—Conversion of thermometric degrees, §§ 1-9.

DEFINITIONS OF CHEMICAL TERMS, §§ 10-12.

EQUIVALENTS—Atomic theory—Combination by volume, §§ 18-15.

AFFINITY—Combination—Decomposition, §§ 16, 17.

NOMENCLATURE AND NOTATION—Symbols—Formulæ—Equations, §§ 18, 19.

PHENOMENA RELATING TO THE PHYSICAL CONDITION OF BODIES—Solution—Crystallization—Forms of crystals—Isomorphism—Dimorphism—Water of constitution and crystallization—Efflorescence—Diffusion of gases, §§ 20-22.

CHEMICAL MANIPULATION.

APPARATUS FOR PREPARATION OF GASES WITH THE AID OF HEAT—Iron retorts—Flasks—Corks—Tubing—Safety-tubes—Funnel-tubes, § 23.

METHOD OF FITTING UP APPARATUS FOR THE GENERATION OF GASES—Operations with corks—Cork-borers—Operations with tubing—Lutes, §§ 24-26.

APPARATUS FOR GENERATION OF GASES AT ORDINARY TEMPERATURES—Woulfe's bottles, § 27.

ARRANGEMENTS FOR PURIFYING GASES—Washing-bottles—Caoutchouc connectors—Drying-tubes, § 28.

APPARATUS FOR COLLECTING GASES—Gas-holder—Gas-bags and bladders—Pneumatic trough—Mercurial trough—Gas-cylinders—Gas-jars—Collection over water and mercury—Collection by displacement, §§ 29, 31.

COMBUSTION OF GASES—Glass-jets—Detonation of gases—Eudiometers, § 32.

COMBUSTION IN GASES—Deflagrating spoons, § 33.

TRANSFERENCE OF GASES—§ 34.

MEASUREMENT OF GASES—Graduated jars and tubes—Precautions in measuring, § 35.

SOLUTION OF GASES—Woulfe's apparatus—Absorption of gases by reagents—Liebig's potassa-apparatus—Pipette, § 36.

CONDENSATION OF GASES—Faraday's tubes—Thilorier's apparatus—Liquefaction and solidification of carbonic acid—Natterer's apparatus, § 37.

- DISTILLATION AND SUBLIMATION**—Theory of the process—Distillation at high temperatures—Stills—Worms—Liebig's condenser—Receivers—Frigorific mixtures—Distillation at lower temperatures, but above 212°—Retorts—Flasks for distillation—Adapters—Joints—Application of heat in distillation—Sand-bath—Precautions in distillation—Distillation at temperatures below 212°—Water-bath—Determination of boiling-points—Fractional distillation—Sublimation, §§ 38-44.
- DISINTEGRATION**—Pestle and mortar—Crushing mortar—Pulverization—Levigation—Granulation—Precipitation of metals, §§ 45, 46.
- SOLUTION—INFUSION—DIGESTION**—Dishes—Beakers—Flasks—Stirrers—Solution on a small scale—Lixiviation—Percolators—Saturation, §§ 47-49.
- FILTRATION**—Funnels—Filtering-paper—Filters—Precautions in filtering—Edulcoration—Syringe-bottle—Decantation—Siphon—Pipette—Separation of liquids—Separating-funnel, §§ 50-52.
- EVAPORATION**—Spontaneous evaporation—Evaporation *in vacuo*—Water-bath—Oil-bath—Evaporation below ebullition—Evaporation at the boiling-point—Evaporation to dryness—Desiccation—Air-bath—Aspirator—Deliquescence—Drying-tiles, §§ 53, 54.
- CRYSTALLIZATION; by solution; by fusion**—Means of promoting crystallization—Crystallization by vaporization, §§ 55, 56.
- IGNITION**—Precautions in heating crucibles, &c.—Crucible-jacket—Ignition in qualitative analysis, § 57.
- FUSION**—Fluxes—Black flux—Action of fluxes—Crucibles—Precautions in fusion, §§ 58, 59.
- SOURCES OF HEAT IN THE LABORATORY**—Lamps—Roaring-lamp—Berzelius and Mitscherlich's lamps—Argand oil-lamp—Gas-burners—Gauze-burner—Furnaces—Drying-closet—Black's furnace—Muffle—Combustion-furnace—Charcoal-chauffer, §§ 60, 61.
- USE OF THE BLOWPIPE**—Black's blowpipe—Blowpipe-lamps—Blowpipe-apparatus—Charcoal supports—Blowpipe-reagents—Intumescence—Decrepitation—Deflagration—Detonation—Incandescence—Structure of the blowpipe-flame—Reduction on Charcoal—Incrustation—Roasting—Colored beads—Colored flames, §§ 62-66.
- GLASSBLOWING**—Table-blowpipe—Herepath's blowpipe—Rose's spirit-blowpipe—Closure of tubes—Sealing of tubes—Glass bulbs—Arsenic tubes—Combustion-tubes, § 67.

ELEMENTARY CHEMISTRY.

- CLASSIFICATION OF ELEMENTS**—Metals and non-metallic substances—Table of symbols and equivalents, § 68.
- OXYGEN**—Oxides—Ozone, §§ 69-72.
- HYDROGEN**—Precautions in preparing hydrogen—Purification, §§ 73, 74.
- WATER**—Circumstances under which water is formed—Action of spongy platinum on gaseous mixtures—Oxyhydrogen blowpipe—Drummond light—Hemming's jet—Synthesis and analysis of water—Ice—Steam—Hydrates—Water from different sources—Hard and soft waters—Mineral waters—Distillation of water—Binoxide of hydrogen, §§ 75-79.
- NITROGEN**—Nitrous oxide—Nitric oxide—Nitrous acid—Peroxide of nitrogen, §§ 80-84.
- NITRIC ACID**—Anhydrous nitric acid—Hydrated nitric acid—Nitrification—Preparation of nitric acid of commerce—Nitrates—Action of nitric acid upon organic substances—Uses, §§ 85, 86.
- ATMOSPHERIC AIR**—Analysis of air—Foreign matters existing in air—Determination of water and carbonic acid—Air merely a mixture, not a combination, §§ 87, 88.

- NITROGEN AND HYDROGEN**—Amidogen—Amides, § 89.
- AMMONIA**—Circumstances under which ammonia is formed—Solution of ammonia—Ammonium—Amalgam of ammonium—Ammonium-theory of Berzelius, §§ 90–92.
- CHLORINE**—Bleaching—Disinfecting—Hypochlorous acid—Euchlorine—Chlorous acid—Peroxide of chlorine—Chloric acid—Chlorates—Chlorochloric acid—Perchloric acid—Chloroperchloric acid—Millon's views, §§ 93–95.
- HYDROCHLORIC ACID**—Solution of hydrochloric acid—Uses—Nitro-hydrochloric acid—Researches of E. Davy and Gay-Lussac—Chloride of nitrogen—Chlorides of the metals, §§ 96, 97.
- BROMINE**—Bromic acid—Hydrobromic acid—Chloride of bromine—Metallic bromides, §§ 98, 99.
- IODINE**—Uses of Iodine—Iodic acid—Periodic acid—Hydriodic acid—Iodide of Nitrogen—Chlorides of iodine—Bromides of iodine—Metallic iodides—Speculations of Dumas—Triads of elements, §§ 100, 101.
- FLUORINE**—Hydrofluoric acid—Metallic fluorides, § 102.
- SULPHUR**—Allotropy—Uses of sulphur, § 103.
- SULPHUR AND OXYGEN**—Hyposulphurous acid—Sulphurous acid—Uses of sulphurous acid—Hyposulphuric acid, § 104.
- SULPHURIC ACID**—Conditions of its formation—Anhydrous sulphuric acid—Nordhausen sulphuric acid—Oil of vitriol—Manufacture of oil of vitriol—Theory of the process—Impurities of oil of vitriol—Other Hydrates of sulphuric acid—Sulphates—Uses of sulphuric acid, § 105.
- BINARY THEORY OF ACIDS**, § 106.
- TRITHIONIC ACID**—Tetrathionic acid—Pentathionic acid, § 107.
- SULPHUR AND HYDROGEN**—Pentasulphide of hydrogen—Hydrosulphuric acid—Sulphur and nitrogen—Nitrosulphuric acid—Sulphate of nitric oxide, §§ 108, 109.
- SULPHUR AND CHLORINE**—Subchloride of sulphur—Chloride of sulphur—Sulphur and bromine—Sulphur and iodine—Metallic sulphides—Sulphur-acids—Sulphur-bases—Sulphur-salts, § 110.
- SELENIUM**—Oxide of selenium—Selenious acid—Selenic acid—Seleniuretted hydrogen—Chlorides of Selenium—Bromides of Selenium—Sulphides of Selenium—Metallic Selenides, §§ 111, 112.
- PHOSPHORUS**—White phosphorus—Amorphous phosphorus—Impurities of phosphorus—Uses of phosphorus, § 113.
- PHOSPHORUS AND OXYGEN**—Suboxide of phosphorus—Hypophosphorous acid—Phosphorous acid, § 114.
- PHOSPHORIC ACID**—Anhydrous phosphoric acid—Metaphosphoric, pyrophosphoric, and common phosphoric acids—Phosphates—Fleitmann and Henneberg's salts, § 115.
- PHOSPHORUS AND HYDROGEN**—Solid, liquid, and gaseous phosphuretted hydrogen—Terchloride of phosphorus—Pentachloride of phosphorus—Oxychloride—Chlorosulphide—Bromides and iodides of phosphorus—Phospham—Phosphamide—Sulphides and selenides of phosphorus—Phosphides, §§ 116, 117.
- CARBON**—Diamond—Graphite—Coal—Origin and formation of coal—Peat—Lignite—Pit-coal—Cannel coal—Pitch-coal—Cubical coal—Splint-coal—Caking coal—Anthracite—Jet—Decomposition of coal—Coal fires—Inorganic constituents of coal—Valuation of fuel—Proximate and ultimate analysis of coal, §§ 118–120.

ARTIFICIAL VARIETIES OF CARBON—Coke—wood—charcoal—*Charbon-roux*—Cylinder-charcoal—Tests of the quality of charcoal—Lampblack—Animal-charcoal—Ivory-black—Decolorizing and disinfecting properties of charcoal—General properties of carbon—Uses of carbon, §§ 121, 122.

CARBON AND OXYGEN—Carbonic oxide—Chlorocarbonic acid—Carbonic oxide series—Carbonic acid—Liquid and solid carbonic acid—Determination of the composition of carbonic acid—Carbonates—Uses of carbonic acid—Aerated waters—Fire-annihilator, §§ 123, 124.

LIGHT CARBURETTED HYDROGEN—Marsh-gas—Fire-damp—Explosions in coal-mines—Davy's safety-lamp—Coal-gas—Valuation of coal-gas—Manufacture of coal-gas—Analysis of coal-gas—Oil-gas—Water-gas, §§ 125–128.

OLEFIANT GAS—Bicarburetted hydrogen of Faraday, § 129.

Cyanogen—Cyanogen series—Mellon, § 130.

Chlorides of carbon—Bisulphide of carbon—Carbides, §§ 131–133.

BORON—Boracic acid—Lagoons—Borates—Boron and nitrogen—Terchloride of Boron—Terfluoride of boron—Sulphide of boron, §§ 134, 135.

SILICON—Silicic acid—Rock-crystal—Opal—Silicates—Uses of silicic acid, §§ 136, 137.

GLASS—Relations of the different ingredients in glass—Devitrification—Materials for glass-making—Varieties of glass—Colored glasses—Artificial gems—Enamels, § 138.

Silicon and hydrogen—Terchloride of silicon—Silicon and bromine—Terfluoride of silicon—Hydrofluosilicic acid—Silicon and sulphur—Chlorosulphide of silicon, § 139.

THE METALS—General considerations, § 140.

POTASSIUM—Suboxide of potassium—Potassa—Hydrate of potassa—Uses of potassa, §§ 141–143.

NITRATE OF POTASSA—Occurrence in nature—Conditions of its formation—Nitric acid—Artificial production of nitrates—Saltpetre-plantations—Preparation and purification of nitre—Uses of nitre—Examination (refraction) of nitre—Gay-Lussac's method—Pelouze's method, §§ 144–148.

GUNPOWDER—Theoretical considerations—Most advantageous composition—Gunpowder of different countries—Manufacture of gunpowder—The ingredients—Nitre—Sulphur—Charcoal—Theoretical considerations respecting *charbon roux*—Pulverization and mixture of the ingredients—Revolutionary process—Granulation of the powder—Waltham Abbey process—Champy process—Glazing—Desiccation—Properties of gunpowder, § 149.

Nitrite of potassa—Chlorate of potassa—Uses—Lucifer matches—Percussion powder—Perchlorate of potassa—Hypochlorite of potassa—Eau de Javelle—Bromate, iodates, and periodate of potassa, §§ 150–154.

Sulphate of potassa—Bisulphate of potassa—Phosphates of potassa, § 155.

CARBONATE OF POTASSA—Impurities of commercial potashes—Pearlash—Bicarbonate of potassa—Silicates of potassa, §§ 156, 157.

Peroxide of potassium—Chloride, bromide, and iodide of potassium—Valuation of iodide of potassium—Fluoride of potassium, §§ 158, 159.

Sulphide of potassium—Hydrosulphate of sulphide of potassium—Bisulphide and polysulphides of potassium—Hepar sulphuris—Theory of the preparation of milk of sulphur—Silicofluoride of potassium, §§ 160, 161.

SODIUM—Minerals containing sodium—Suboxide of sodium, § 162.

SODA—Hydrate of soda—Nitrate of soda—Hypochlorite of soda—Chloride of soda—Bleaching liquid of Labarraque—Chlorate of soda—Hyposulphite and sulphite of soda—Glauber's salt—Bisulphate of soda, §§ 163–167.

PHOSPHATES OF SODA—Triphosphate—Common phosphate—Acid phosphate—Pyrophosphates—Metaphosphate—Fleitmann and Henneberg's salts, § 168.

CARBONATE OF SODA—Barilla—Blanquette—Salicor—Kelp—Manufacture of carbonate of soda from common salt—Balling process—Composition of black ash and soda waste—Economic relations of Leblanc's process—Properties and uses of carbonate of soda—Carbonate of potassa and soda—Sesquicarbonate and bicarbonate of soda, §§ 169–172.

BORATE OF SODA—Borax—Tincal—Refining of Tincal—Manufacture of Borax—Octohedral borax—Vitrified borax—Uses of borax—Valuation of tincal—Silicates of soda—Peroxide of sodium, §§ 173, 174.

CHLORIDE OF SODIUM—Extraction of salt, in England, France, Germany, and Russia—Graduating works—Schlotage—Socage—Uses of chloride of sodium—Salt-glazing, § 175.

Bromide, iodide, and fluoride of sodium—Sulphides of sodium—Lapis lazuli—Ultramarine, § 176.

LITHIUM—Lithia—Extraction of lithia from lepidolite—Salts of lithia, § 177.

AMMONIUM—Oxide of ammonium—Nitrite, nitrate, sulphite, sulphate, bisulphate, and phosphates of ammonia—Microcosmic salt—Carbonate of ammonia—Bicarbonate of ammonia—Phosphate of soda and ammonia, §§ 178–181.

CHLORIDE OF AMMONIUM—Manufacture of sal-ammoniac—Uses—Sulphides of ammonium—Hydrosulphate of sulphide of ammonium—Liquor fumans Boylii, §§ 182–184.

BARIUM—Baryta—Hydrate of baryta—Nitrate, chlorate, sulphite, sulphate, seleniate, phosphates, carbonates, and borates of baryta, §§ 185–189.

Binoxide of barium—Chloride of barium—Sulphides of barium—Silicofluoride of barium, §§ 190–192.

STRONTIUM—Strontia—Hydrate, nitrate, sulphate, and carbonate of strontia—Binoxide of strontium—Chlorides of strontium, § 193.

CALCIUM—Lime—Lime-burning—Quicklime—Slaking of lime—Hydrate of lime—Uses—Mortar—Theory of the hardening of mortar—Hydraulic mortars and cements—Modus operandi of cement—Roman cement—Puzzolano—Ransome's vitrified cement—Hydraulic mortar of Tournay, §§ 194, 195.

Nitrate of lime—Hypochlorite of lime—Chloride of lime—Manufacture of bleaching-powder—Uses of chloride of lime—Sulphite and bisulphite of lime—Sulphate of lime—Gypsum—Uses of sulphate of lime—Plaster of Paris—Stucco, §§ 196–198.

PHOSPHATE OF LIME—Bone-earth—superphosphate of lime as manure—Carbonate of lime—Natural varieties—Petrifying springs—Stalactites—Uses of carbonate of lime—Carbonate of lime and soda—Binoxide of calcium, §§ 199, 200.

Chloride of calcium—Oxychloride of calcium—Fluorspar—Sulphides of calcium—Phosphide of calcium, §§ 201, 202.

MAGNESIUM—Magnesia—Hydrate of magnesia—Nitrate and hypochlorite of magnesia—Sulphate of magnesia—Manufacture of Epsom salts—Sulphate of magnesia and potassa—Sulphate of magnesia and ammonia, §§ 203–205.

Phosphates of magnesia—Triple phosphate—Ammoniac-magnesian phosphate—Phosphate of magnesia and potassa—Carbonate of magnesia—Magnesia alba—Heavy carbonate—Dolomite—Borates and silicates of magnesia—Meerschaum, talc, asbestos—Chloride of magnesium—Sulphide of magnesium, §§ 206–208.

ALUMINUM—Alumina—Corundum—Ruby, emerald, amethyst, sapphire—Hydrates of alumina—Aluminates—Nitrate of alumina, § 209.

SULPHATES OF ALUMINA—ALUMS—Common alum—Manufacture of alums—Alum-stone—Russum alum—Alum-slate—Beaching of alum—Cubical alum—Uses of alum—Sulphate-alum—Ammonia-alum—Phosphates of Alumina—Wavellite, §§ 210, 211.

MINERALS OF ALUMINA—Feldspars—Pumice-stone—Mica—Hornblende—Basalt—Glaucous—Clays—Kaolin—Properties and varieties of clay—Earthenware and porcelain—Glazing—Coloured glazes—Fire-bricks—Crucibles—Manufacture of English porcelain—Sèvres China—*Porcelaine tendre*—Berlin porcelain, §§ 212, 213.

Alumina with chlorine, fluorine, and sulphur, § 214.

GLUCINUM—Glucina—Preparation, from emerald of Limoges—Salts of glucina—Reactions of glucina, § 215.

THORIUM—Thoria—Reactions of thorina, § 216.

YTRIAM, ERBICUM, and TERBICUM—Ytria—Erbia—Terbia—Extraction from gadolinita—Salts of Ytria, erbia, and terbia—Reactions of Ytria, erbia, and terbia, § 217.

CERIAM, LANTHANICUM, and DIDYMIUM—Extraction from cerite—Oxide of cerium—Salts of oxide of cerium—Sesquioxide, chloride, and sulphide of cerium—Oxides and salts of lanthanum and Erymium—Reactions of the oxides of cerium, lanthanum, and Erymium, § 218.

ZIRCONIUM—Zirconia—Extraction from hyacinth—Salts and reactions of zirconia, § 219.

CHROMIUM—Oxide and sesquioxide of chromium—Nitrate and sulphate of sesquioxide of chromium—Chrome-alums—Carbonate of sesquioxide of chromium—Protosessquioxide of chromium, §§ 220, 221.

Chromium acid—Chromate, bichromate, and terchromate of potassa—Chlorochromate of potassa—Chromates of soda, ammonia, and sesquioxide of chromium—Perchromic acid—Sesquichloride, chloride, and sesquichloride of chromium—Chlorochromic acid—Fluoride and sulphides of chromium, §§ 222, 223.

URANIUM—Minerals containing uranium—Suboxide and oxide of uranium—Sulphate of oxide of uranium—Protosessquioxide and sesquioxide of uranium—Nitrate and sulphate of sesquioxide of uranium—Extraction of uranium from pitchblende—Uranate of potassa—Chlorides of uranium—Reactions of sesquioxide of uranium, § 224.

IRON—Preparation of pure iron—General properties of iron—Passive state—Oxide of iron—Kinetic of oxide of iron—Green vitriol—Manufacture of green vitriol—Uses—Composition of oxide of iron, §§ 225–227.

Sesquioxide of iron—Uses of sesquioxide of iron—Nitrate and sulphates of sesquioxide of iron—Iron-alum—Phosphate and silicates of sesquioxide of iron, § 228.

Magnetic oxide of iron—Ferric acid—Ferrates—Nitride, chloride, sesquichloride, and bromides of iron—Iodide and sesqui-iodide of iron, §§ 229, 230.

Sulphides of iron—Sesquisulphide of iron—Magnetic pyrites—Bisulphide of iron—Iron-pyrites—Subsulphide of iron—Iron with carbon, boron, and silicon, §§ 231, 232.

MANUFACTURE OF IRON—Meteoric stones—Ores of iron—Manufacture of iron—Preparation of the ores—Extraction of the metal—Manufacture of pig-iron—Blast furnace—Theory of the reduction of iron—Conversion of pig-iron into bar-iron—Refining—Cast-iron—Iron—Puddling—Different varieties of cast-iron—Wrought-iron—Steel—Natural steel—Kiln-fired steel—Shear-steel—Cast-steel—Tempering of steel—Kilny of iron-ores, § 233.

MANGANESE—Oxide of manganese—Sulphate of manganese—Phosphate, carbonates, and silicates of manganese—Sesquioxide of manganese—Sulphate of the sesquioxide—Manganese-alums—Red oxide of manganese—Binoxide of manganese—Uses of binoxide of manganese, §§ 234–236.

- Manganic acid—Manganates—Chameleon mineral—Permanganic acid—Permanganate of potassa, &c.—Chloride, sesquichloride, and sulphides of manganese, §§ 237, 238.**
- ZINC—Purification of commercial zinc—Granulated zinc—Suboxide and oxide of zinc—Zinc-white—Nitrate, sulphate, carbonate, and silicate of zinc—Binoxide of zinc, §§ 239-241.**
 Chloride and sulphide of zinc—Metallurgy and uses of zinc—Assay of ores of zinc, §§ 242, 243.
- NICKEL—Preparation of pure nickel—Oxide of nickel—Nitrate, sulphate, and carbonate of nickel—Sesquioxide of nickel, §§ 244, 245.**
 Chloride and sulphide of nickel—Metallurgy of nickel—Minerals containing nickel—Extraction of nickel from speiss, §§ 246, 247.
- COBALT—Oxide of cobalt—Nitrate, sulphate, and carbonates of cobalt—Sesquioxide of cobalt—Intermediate oxides of cobalt—§§ 248, 249.**
 Chlorides and sulphides of cobalt—Technical history of cobalt—Zaffre—Smalt—Thénard's blue, §§ 250, 251.
- VANADIUM—Oxide and binoxide of vanadium—Vanadic acid—Terechloride and bisulphide of vanadium—Reactions of vanadium, § 252.**
- CADMIUM—Oxide of cadmium—Nitrate, sulphates, and carbonates of cadmium—Chloride and sulphide of cadmium, § 253.**
- COPPER—Suboxide of copper—sulphate of suboxide of copper—Oxide of copper—Verditer—Ammoniacal oxides of copper, §§ 254, 255.**
 Nitrate and ammonio-nitrate of copper—Sulphate of copper—Manufacture of blue vitriol—Ammoniated sulphate of copper—Uses of blue vitriol—Tests for impurities—Basic sulphates of copper—Ammonio-sulphate of copper—Carbonates of copper—Malachite—Silicate of copper, § 256.
 Binoxide of copper—Cupric acid—Copper and hydrogen—Copper and nitrogen—Chlorides of copper—Oxychlorides—Brunswick green, §§ 257, 258.
 Sulphides of copper—Copper-glance—Sulphide of copper—Oxysulphide—Copper pyrites—Variegated copper ore—Phosphides of copper, § 259.
METALLURGY OF COPPER—Ores of copper—Smelting of copper ores—Brankart's process—Process of Rivot and Phillips—Napier's process—Uses of copper—Engraving—Alloys of copper and zinc—Brass, &c.—Alloys of copper and tin—Bronze—gun-metal—Casting of guns—Bell-metal, &c.—German silver—Tinned copper—Pins—Assay of copper-ores, §§ 260-262.
- BISMUTH—Purification of commercial bismuth—Suboxide and teroxide of bismuth—Nitrates of bismuth—Flake-white—Sulphates and carbonate of bismuth—Bismuthic acid, §§ 263, 264.**
 Terechloride of bismuth—Oxychloride of bismuth—Pearl-white—Sulphides of bismuth—Metallurgy of bismuth—Minerals of bismuth—Extraction from its ores—Uses—Fusible alloy—Assay of ores of bismuth, §§ 265, 266.
- GOLD—Preparation of pure gold—Oxide of gold—Hyposulphite of gold and soda—Purple of Cassius—Auric acid—Aurates—Fulminating gold—Aurosulphite of potassa—Chloride and terechloride of gold—Aurum potabile—Aurochlorides—Sulphides of gold, §§ 267-269.**
METALLURGY OF GOLD—Distribution—Alluvial gold—Extraction of gold—Gold-washing—Gold-dust—Extraction by fusion—Amalgamation of gold-ores—Refining of gold—Parting by sulphuric acid—Gold for coin—Jeweller's gold—Gold-leaf—Gilding—Electro-gilding—Assay of alloys of gold—Touchstone—Assay by cupellation—

- Quartation—Determination of gold in auriferous sand—Assay of ores containing gold—Calculation of gold in gold quartz, §§ 270, 271.
- PLATINUM**—Purification of commercial platinum—Malleable platinum—Spongy-platinum—Platinum-black—Circumstances under which platinum vessels are damaged—Oxide of platinum—Binoxide of platinum—Fulminating platinum—Platinates—Nitrate and sulphate of binoxide of platinum—Platinum with hydrogen, §§ 272, 273.
- Protochloride of platinum—Ammoniated chloride—Green salt of Magnus—Reiset's platinum-bases—Platosammonium—Gros's base—Raewaky's base—Bichloride of platinum—Preparation of bichloride of platinum from platinum-residues—Double-salts of bichloride of platinum with other chlorides—Sulphides of platinum, §§ 274, 275.
- METALLURGY OF PLATINUM**—Extraction of platinum from the ore—Uses of platinum, § 276.
- PALLADIUM**—Uses—Oxide and binoxide of palladium—Chlorides of palladium—Reactions, § 277.
- RHODIUM**—Oxides and chlorides of rhodium—Reactions, § 278.
- IRIDIUM**—Oxides of iridium—Chlorides—Reactions of iridium, § 279.
- OSMIUM**—Oxide, sesquioxide, and binoxide of osmium—Osmious acid—Osmic acid—Chlorides of osmium—Reactions, § 280.
- RUTHENIUM**—Oxides of ruthenium—Ruthenic acid—Chlorides of ruthenium—Reactions—Relations between the metals existing in platinum-ores, § 281.
- Analysis of the ores of platinum, § 282.
- TIN**—Preparation of pure tin—Oxide of tin—sulphate and nitrate of oxide of tin—Stannic acid—Stannates—Metastannic acid—Metastannates, §§ 283-285.
- Chloride of tin—Oxychloride of tin—Valuation of chloride of tin—Bichloride of tin—Chlorostannates—Sulphide and bisulphide of tin—Mosaic gold, § 286.
- METALLURGY OF TIN**—Ores of tin—Smelting of tin ores—Extraction of tungsten from the ores of tin—Refining of tin by liquation—Uses of tin—Tinfoil—Manufacture of tin-plates—Alloys of tin—Assay of tin-ores, § 287.
- ANTIMONY**—Purification of antimony—Suboxide of antimony—Teroxide of antimony—Nitrate and sulphates of teroxide of antimony—Anomalous composition of the salts of this base, §§ 288, 289.
- Antimonic acid—Antimonates of potassa, soda, ammonia, and teroxide of antimony (antimonious acid)—Metantimonic acid—Metantimonates and bi-metantimonates of potassa, soda, and ammonia, § 290.
- Antimoniuretted hydrogen—Terchloride of antimony—Oxychlorides of antimony—Pentachloride of antimony—Bromide, iodide, and fluoride of antimony, § 291.
- Tersulphide of antimony—Glass of antimony—Crocus—Liver of antimony—Pentasulphide of antimony—Sulphantimonates—Kermes mineral—Alloys of antimony, §§ 292, 293.
- METALLURGY OF ANTIMONY**—Minerals of antimony—Extraction of antimony from its ores—Assay of ores of antimony—Pharmaceutical preparations of antimony, §§ 294, 295.
- ARSENIC**—Fly-powder—Arsenious acid—Arsenites—Scheele's green—Schweinfurt green—Arsenic acid—Arsenates, §§ 296-299.
- Arseniuretted hydrogen—Terchloride of arsenic—Sulphides of arsenic—Realgar—Yellow orpiment—Sulpharsenious acid—Sulpharsenic acid—Arsenides—Pharmaceutical preparations of arsenic, §§ 300, 301.

TUNGSTEN—Wolfram—Bioxide of tungsten—Tungstic acid—Blue oxide of tungsten—Tungstates—Chlorides, sulphides, and phosphides of tungsten—Reactions of tungsten, § 802.

MOLYBDENUM—Oxide and bioxide of molybdenum—Molybdic acid—Deposited with phosphoric acid—Chlorides and sulphides of molybdenum—Reactions, § 808.

TELLURIUM—Tellurous acid—Telluric acid—Telluretted hydrogen—Chlorides and sulphides of tellurium—Reactions of tellurium, § 804.

TITANIUM—Minerals containing titanium—Extraction from rutile—Oxide and sesquioxide of titanium—Titanic acid—Nitrides, chlorides, and sulphide of titanium—Reactions, § 805.

MERCURY—Purification of commercial quicksilver—Suboxide of mercury—Nitrates, sulphate, and chromate of suboxide of mercury, §§ 806, 807.

Oxide of mercury—Oxy-amidide of mercury—Salts of oxy-amidide of mercury—Nitrates and sulphates of oxide of mercury—Turbit mineral—Carbonates of mercury, § 808.

Nitride of mercury—Subchloride of mercury—Preparation of calomel—Chloride of mercury—Double compounds of chloride of mercury—Uses of corrosive sublimate—Oxychlorides of mercury—Amido-chloride—White precipitate, §§ 809, 810.

Bromides of mercury—Iodides of mercury—Sulphides of mercury—Vermilion—Manufacture of vermilion—Cinnabar, §§ 811, 812.

AMALGAMS of potassium, sodium, and ammonium—Amalgams of iron, zinc, and bismuth—Amalgam for electrical machines—Amalgam of gold—Preparation of powdered gold—Amalgams of platinum, copper, and tin—Silvering of looking-glasses—Amalgams of lead and silver, § 818.

METALLURGY OF MERCURY—Occurrence in nature—Extraction of mercury from its ores—Assay of ores of mercury—Pharmaceutical preparation of mercury, § 814.

LEAD—Preparation of pure lead—Lead pyrophorus—Saturn's tree—Suboxide of lead—Massicot—Litharge—Uses—Nitrites, nitrates, and sulphate of lead—Carbonate of lead—Manufacture of white lead—Uses and adulterations—Silicates of lead—Chromates of lead—Chrome-yellow, §§ 815-817.

Binoxide of lead—Plumbates—Minium—Uses of red-lead—Chloride and oxychlorides of lead—Bromide and iodide of lead—Sulphide and selenide of lead, §§ 818-820.

METALLURGY OF LEAD—Ores of lead—Smelting of galena—Refining of argentiferous lead—Pattinson's process—Cupellation—Uses of lead—Alloys—Plumber's solder—Tea-lead—Type-metal—Lead-shot—Manufacture of shot—Assay of galena, §§ 821, 822.

SILVER—Preparation of pure silver—Suboxide of silver—Oxide of silver—Fulminating silver—Nitrite of silver—Nitrate of silver—Lunar-caustic—Ammonio-nitrate of silver—Uses of nitrate of silver—Hyposulphate, sulphate, and carbonate of silver—Binoxide of silver, §§ 823-825.

CHLORIDE OF SILVER—Reduction of silver from the chloride—Bromide, iodide, and fluoride of silver—Sulphide and carbides of silver, § 826.

METALLURGY OF SILVER—Ores of silver—Extraction of silver—Extraction by Cupellation—Amalgamation-process—Method adopted at Freiberg—American amalgamation process—Mexican method of extraction, § 827.

TECHNICAL HISTORY OF SILVER—Alloys of silver and copper—Standard silver—alloys of silver and gold—Plating—Electroplating—Silvering upon glass—Assay of silver ores, § 828.

TANTALUM—Oxide of tantalum—Tantalic acid—Chloride and sulphide of tantalum—Niobium—Niobic acid—Chloride and sulphide of Niobium—Pelopium—Pelopic acid—Chloride and sulphide of pelopium—Ilmenium—Ilmenic acid—Extraction of tantalum, niobium, and pelopium from tantalites and yttrio-tantalites, § 329.

PHYSICAL PROPERTIES OF THE METALS, § 330.

ANALYTICAL CHEMISTRY.

Definitions of qualitative and quantitative, proximate and ultimate analysis—Apparatus and reagents used in qualitative analysis, §§ 331–333.

ANALYTICAL CLASSIFICATION OF METALS, § 334.

REACTIONS OF THE OXIDES OF THE FIRST GROUP—Potassa—Soda—Oxide of ammonium, § 335.

REACTIONS OF THE OXIDES OF THE SECOND GROUP—Baryta—Strontia—Lime, Magnesia, § 336.

REACTIONS OF THE OXIDES OF THE THIRD GROUP—Alumina—Sesquioxide of Chromium—Oxide and sesquioxide of iron—Oxides of Cobalt, Nickel, Manganese, and Zinc, § 337.

REACTIONS OF THE OXIDES OF THE FOURTH GROUP—Oxides of Mercury, Copper, and Cadmium—Teroxide of Gold—Binoxide of Platinum—Oxide and Binoxide of tin—Teroxide of Antimony—Antimonious Acid—Arsenious and Arsenic Acids, § 338.

REACTIONS OF THE OXIDES OF THE FIFTH GROUP—Oxide of Lead, Suboxide of Mercury, Oxide of Silver, § 339.

ANALYTICAL CLASSIFICATION OF INORGANIC ACIDS, § 340.

REACTIONS OF THE ACIDS OF THE FIRST GROUP—Sulphuric, Phosphoric, Boracic, and Silicic acids, § 341.

REACTIONS OF THE ACIDS OF THE SECOND GROUP—Sulphurous, Chromic, Hydrofluoric, and Carbonic acids, § 342.

REACTIONS OF THE ACIDS OF THE THIRD GROUP—Hydrochloric, Hydrobromic, Hydriodic, Hydrosulphuric, Hydrocyanic, Hydrosulphocyanic, Hydroferrocyanic, and Hydroferricyanic acids, § 343.

REACTIONS OF THE ACIDS OF THE FOURTH GROUP—Nitric, Chloric, and Hypochlorous acids, § 344.

ANALYTICAL CLASSIFICATION OF ORGANIC ACIDS, § 345.

REACTIONS OF ACIDS OF THE FIRST GROUP—Tartaric, Tannic, and Gallic Acids, § 346.

REACTIONS OF ACIDS OF THE SECOND GROUP—Citric and Uric Acids, § 347.

REACTIONS OF ACIDS OF THE THIRD GROUP—Benzoic, Succinic, and Acetic Acids, § 348.

SYSTEMATIC COURSE OF QUALITATIVE ANALYSIS—Preparation of substances for analysis—Preliminary examination for bases—Solution of substances for analysis—Treatment with general reagents—Analytical tables for detection of bases—Preliminary examination for acids—General examination for acids—Tables for detection of acids—Special tests for acids, §§ 349–356.

Qualitative analysis of insoluble substance; of alloys and amalgams, §§ 357, 358.

QUANTITATIVE ANALYSIS—Apparatus used in quantitative analysis—Balances, &c., § 359.

OPERATIONS IN QUANTITATIVE ANALYSIS—Weighing—Solution—Evaporation—Ignition—Precipitation—Washing of precipitates—Weighing of precipitates—Ignition of precipitates, § 360.

Determination of Oxide of Silver, Suboxide and Oxide of Mercury, and Oxide of Lead—Valuation of Cinnabar, §§ 361–365.

CONTENTS.

- Determination of Teroxide of Bismuth and Oxide of Copper—Wet assay of copper-ores—
Determination of Oxide of Cadmium, Teroxide of Gold, Binoxide of Platinum, Oxide
and Binoxide of Tin, Teroxide of Antimony, Antimonio Acid, Arsenious and Arsenic
Acids, §§ 366-374.
- Determination of Alumina, Sesquioxide of Chromium, Oxide and Sesquioxide of Iron,
Oxides of Cobalt, Nickel, Manganese, and Zinc, §§ 375-382.
- Determination of Baryta, Strontia, Lime, and Magnesia, §§ 383-386.
- Determination of Potassa, Soda, and Oxide of Ammonium, §§ 387-389.
- Determination of Sulphuric, Phosphoric, Boracic, and Silicic Acids, §§ 390-393.
- Determination of Sulphurous, Chromic, Hydrofluoric, Carbonic, and Oxalic Acids, §§ 394,
398.
- Determination of Hydrochloric, Hydrobromic, Hydriodic, and Hydrosulphuric Acids,
§§ 399-402.
- Determination of Nitric and Chloric Acids, §§ 403, 404.
- QUANTITATIVE ANALYSIS; SPECIAL METHODS—Analysis of common salt—Calculation of
analyses, § 405.
- Analysis of common phosphate of soda—Determination of water of crystallization and of
constitution, § 406.
- Analysis of heavy spar, § 407.
- Analysis of Rochelle salt—Separation of potassium and sodium, § 408.
- Analysis of marble, § 409.
- Analysis of limestones—Separation of lime, magnesia, sesquioxide of iron, alumina, and
silica, § 410.
- Analysis of alum—Separation of alumina and potassa, § 411.
- Analysis of chrome-iron ore—Separation of iron and chromium, § 412.
- Analysis of clay—Separation of iron, alumina, silica, lime, and magnesia, § 413.
- Analysis of wavellite—Separation of alumina and phosphoric acid, § 414.
- Analysis of iron-ores—Margueritte's process—Preparation of standard solution of per-
manganate of potassa—Determination of the relative quantities of the oxides of iron,
§ 415.
- Analysis of manganiferous spathic iron-ore—Separation of iron and manganese, § 416.
- Analysis of crystallized sulphate of copper, § 417.
- Analysis of calamine—Separation of cadmium and zinc, § 418.
- Analysis of copper-pyrites—Separation of copper and iron, § 419.
- Analysis of tartar-emetic, § 420.
- Analysis of pewter—Separation of tin, antimony, copper, and bismuth, § 421.
- Analysis of fusible alloy—Separation of tin, lead, and bismuth, § 422.
- Analysis of type-metal—Separation of antimony, lead, and bismuth, § 423.
- Analysis of brass, bronze, and gun-metal—Separation of tin, lead, copper, and zinc, § 424.
- Analysis of German silver—Separation of copper, zinc, and nickel, § 425.
- Analysis of Britannia metal—Separation of tin, antimony, copper, and lead, § 426.
- Analysis of standard silver—Separation of copper and silver—Centigrade determination
of silver, § 427.
- Analysis of standard gold—Separation of gold, silver, and copper, § 428.
- Analysis of amalgams—Separation of mercury and zinc—Separation of mercury and tin,
§§ 429, 430.
- Analysis of speiss-cobalt—Separation of arsenic, cobalt, nickel, and iron, § 431.
- Valuation of manganese-ores, § 432.
- Chlorimetry—Valuation of chloride of lime, § 433.
- Alkalimetry—Valuation of potash and soda—Fresenius and Will's alkalimetric appa-
ratus, § 434.

- Acidimetry—Estimation of the strength of dilute nitric acid, § 435.
Analysis of gunpowder, § 436.
Analysis of glass—Analysis of insoluble silicates—Determination of alkalis in insoluble silicates—Brunner's method of analyzing silicates, § 437.
Analysis of cast-iron, § 438.
Analysis of ultramarine, § 439.
Separation of chlorine, bromine, and iodine, § 440.
Analysis of mineral waters—Clark's method for determining the hardness of waters, § 441.
Analysis of soils, § 442.
Analysis of the ashes of vegetables, § 443.
Analysis of the ashes of animal substances, § 444.

LIST OF ILLUSTRATIONS.

FIGS.	PAGE
1, 2. Hydrometer	35
3. Globe to determine the density of vapors	37
4. Cube	58
5. Regular octohedron	ib.
6. Rhombic dodecahedron	ib.
7, 8. Right square prisms	ib.
9, 10. Right square-based octohedron	ib.
11. Right rectangular prism	54
12. Right rhombic prism	ib.
13. Rectangular-based octohedron	ib.
14. Right rhombic-based octohedron	ib.
15. Oblique rectangular prism	ib.
16. Oblique rhombic prism	ib.
17. Oblique rectangular-based octohedron	ib.
18. Oblique rhombic-based octohedron	ib.
19. Doubly oblique rectangular prism	55
20. Doubly oblique rhombic prism	ib.
21. Doubly oblique rectangular-based octohedron	ib.
22. Doubly oblique rhombic-based octohedron	ib.
23. Regular six-sided prism	ib.
24. Regular dodecahedron	ib.
25. Rhombohedron	ib.
26. Scalene dodecahedron	ib.
27. Cube, solid angles truncated	ib.
28. " " replaced by faces	ib.
29. " original planes nearly obliterated	ib.
30, 31, 32. Hemihedral crystals	ib.
33. Graham's diffusion tube	57
34. Safety tube	60
35. Cork borer	61
36, 37. Bent tubes	62
38, 39. Washing bottles for gas	65
40. Making caoutchouc joint	ib.
41. Siphon eudiometer	71
42. Transferring gases	72
43. Liebig's potassa apparatus	74
44. Pipette	ib.
45. Thilorier's apparatus	75
46. Liebig's condenser	78

FIGS.	PAGE
47. Revert hood	81
48. Sublimation	84
49. Pouring by glass rod	89
50. Washing bottle for solids	92
51. Pipette	93
52. Separating funnel	ib.
53. Evaporation by sulphuric acid	94
54. Desiccating box	95
55. Bunsen's lamp	102
56. Gassé gas-burner	103
57. Ring gas-burner	ib.
58. Combustion furnace	104
59. " " screen	ib.
60. Common blowpipe	105
61. Bick and Wellaston's blowpipe	ib.
62. Nature of flame	106
63. " blowpipe flame	ib.
64. Preparation of hydriodic acid	151
65. Sulphuric acid chamber	160
66. Preparation of carbonic oxide	196
67. Analysis of carbonic acid	200
68. Preparation of bisulphide of carbon	213
69. " of hydrosulphuric acid	227
70. Test-tube holder	297
71. Berin's crucible	ib.
72. Washing bottle	ib.
73. Spirit-lamp	ib.
74. Cork tapers	ib.
75. Sulphureted hydrogen apparatus	ib.
76. Fresenius and Babo's test for arsenic	535
77. Mascé's test for arsenic	536
78. Graduated burette	616
79. Fresenius and Weyl's carbonic acid apparatus	617

INTRODUCTION.

EXPERIMENTAL SCIENCE may be conveniently divided into PHYSICS and CHEMISTRY.

PHYSICAL SCIENCE treats of the changes of matter, without any regard whatever to its internal constitution.

Thus, the laws of gravitation and cohesion, which belong to physical science, only concern matter irrespective of its composition.

CHEMISTRY, on the other hand, makes us acquainted with the composition of different forms of matter, and with the changes which they are capable of inducing in each other.

Water, considered with regard to its *physical* properties, is a colorless, mobile liquid, boiling at 212° , and freezing at 32° , almost incapable of compression, and so forth. *Chemically* speaking, water is described as a compound of so much hydrogen and oxygen, capable of entering into certain combinations, and of inducing certain changes in other forms of matter.

The science of chemistry is usually divided into two branches—*inorganic* and *organic* chemistry. As a convenient mode of classifying our knowledge this division is useful, but as a natural and absolute separation it has no existence; for the two classes of substances, inorganic and organic, so merge into each other—so many so-called organic substances are found capable of being prepared by inorganic methods, that the boundary-line is day by day becoming fainter, and will, perhaps, in time, vanish altogether. Probably one of the safest definitions that can be given of organic chemistry, as distinguished from inorganic, is contained in the statement, that the former branch of the science treats of those substances which are the products, either directly or indirectly, of the vital process in animals or vegetables; and such a definition will be tacitly admitted throughout this work.

SPECIFIC GRAVITY.

§ 1. The specific gravity of a substance is the term used to express the relation which exists between the weights of equal volumes of this substance, and of some standard body arbitrarily selected.

Pure water at the temperature of 60° F. ($15^{\circ}.5$ C.) is the standard to which the specific gravities of solids and liquids are referred, whilst gases are compared with pure and dry atmospheric air.

Since we have here to compare the weights of equal volumes, and as alterations of volume always attend upon variations of temperature and barometric pressure, it is of course highly important that these conditions (the latter of the two, especially in the case of gases) be taken into consideration.

The determination of the specific gravities of substances is an operation of considerable importance to the practical chemist, and it will not, therefore, be out of place to describe, at the outset, the methods of ascertaining the specific gravities of solids, liquids, and gases.

DETERMINATION OF THE SPECIFIC GRAVITY OF A SOLID MASS INSOLUBLE IN WATER.

§ 2. The mass is accurately weighed in the ordinary balance. It is then attached to a fine silver thread, which may be covered with a thin film of wax to prevent variation in weight; or a horsehair, and suspended to the hook at the bottom of the specific-gravity-pan of the balance: the latter is then brought into equilibrium by adding the requisite weights: the surface of the mass having been carefully wetted with a brush to remove all air-bubbles (or, which is better in some cases, having been heated in the water and allowed to cool below the surface), it is now completely immersed in pure water at 60° F. (15° C.), and the balance again brought into equilibrium: the weight which it has been found requisite to remove for this purpose is that of an amount of water equal in volume to the mass: and the specific gravity may now be calculated by the following simple proportion:—

$$\frac{\text{Weight of an equal volume of water}}{\text{Weight of the mass}} :: 1 : x$$

where x will be the specific gravity required.

If the mass be lighter than water, it must be attached to some heavy body of known specific gravity, and the determination conducted with this combination just as with the simple mass, a modification being of course requisite in the calculation.

DETERMINATION OF THE SPECIFIC GRAVITY OF A SOLID MASS SOLUBLE IN WATER.

§ 3. If the substance, the specific gravity of which is required, be soluble in water, the latter is replaced by some other liquid of known specific gravity, which is incapable of acting upon the substance (e.g. Alcohol, glyceric spirit, &c.): the specific gravity is then taken in the usual way, and the result calculated by the following proportion:—

$$\frac{\text{Weight of an equal volume of the liquid employed}}{\text{Weight of the mass}} :: \text{Sp. Gr. of the liquid} : x$$

where x represents the specific gravity of the substance operated upon.

DETERMINATION OF THE SPECIFIC GRAVITY OF A SUBSTANCE IN THE STATE OF POWDER.

§ 4. If the substance be in a state of minute division, it will of course be impracticable to determine its specific gravity by either of the above methods: a pretty close approximation to the truth, however, may be obtained by placing a quantity, say 200 grs. of the powder, in a small dry bottle, previously weighed, and capable of containing a known weight, say 1000 grs. of the liquid to be employed, at 60° F. (15° C.). There should be a mark upon the neck of the bottle, showing the level to which it is to be filled with the liquid. The weight of the powder and bottle having been accurately ascertained, the latter is filled to the required level with the liquid, the excess of which is regulated by the siphon

In general, for practical purposes, it is convenient to refer the specific gravity to 1000, since decimals may then, to a great extent, be dispensed with.

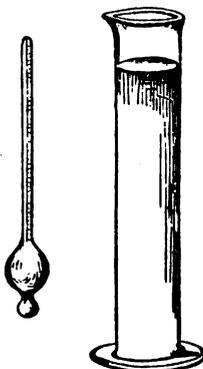
of the solid to be operated upon) at 60° F. (15° C.), and the weight again ascertained. The liquid should be poured upon the powder by small portions at a time, and well agitated, to remove air-bubbles (or, in some cases, it might be slightly heated, and allowed to cool before weighing). By subtracting the weight of the liquid which has been poured into the bottle, from the total weight of the liquid which the latter is known to be capable of containing, we obtain the weight of a volume of liquid equal to that of the powder employed, and from this datum the specific gravity is calculated as usual.

DETERMINATION OF THE SPECIFIC GRAVITY OF A LIQUID.

§ 5. The instrument employed for determining the specific gravity of a liquid is a small light bottle (the weight of which is known), capable of containing a known weight of water at 60° F. (15° C.) when filled to a certain level previously ascertained, and carefully marked. The bottle sold by the instrument-makers for this purpose, is generally provided with a perforated stopper through which the excess of liquid escapes. The operation by which the specific gravity is obtained is exceedingly simple. The bottle is filled to the required level with the liquid to be examined, at the temperature of 60° F. (15° C.), and weighed. (When the temperature of the liquid is below this point, it is generally raised by clasping the bottle in the hand, or immersing it in warm water; if the temperature be higher than 60°, the bottle may be surrounded with a strip of wet blotting-paper, and cooled in a current of air.) To obtain the specific gravity, it is merely necessary to divide the weight of the liquid by the known weight of water which the bottle is capable of containing. (It is scarcely necessary to remark, that the presence of bubbles of air upon the sides of the bottle must be carefully avoided, and that the exterior of the latter must be well wiped before weighing.)

In order to obtain quickly an approximation to the specific gravity of a liquid, an instrument known as the *hydrometer* is frequently employed; it consists of a glass tube of small diameter, forming the stem, to the lower extremity of which two bulbs are attached. The upper of these bulbs is simply filled with air, whilst the lower contains some heavy substance (mercury or shot), the weight of which is regulated according to the purpose for which the hydrometer is intended, being, of course, heavier when the hydrometer is to be employed for liquids of high density. When the hydrometer is placed in any liquid, it will assume an upright position, with more or less of its stem projecting above the surface; it is obvious that, following the ordinary law with regard to floating bodies, the height of the stem above the surface will depend upon the specific gravity of the liquid, and it is only necessary that the stem be graduated, in order that we may at once read off the specific gravity. The zero of the scale is usually obtained by floating the hydrometer in pure distilled water at 60° F. (15° C.), and marking upon its stem (or upon a scale attached to it) the level to which it sinks; the same experiment being repeated with another liquid of known specific gravity, a second starting-point is obtained, and the space between these two points is divided into an arbitrary number of degrees, to which those on all parts of the scale are of course equal. Since the stem of the hydrometer of extensive range would be inconveniently long, separate instruments are adapted to different portions of the scale. In the graduation commonly used in this country, the degrees correspond to grains, and

Fig. 1. Fig. 2.



the specific gravity is thus read off at once. This method is adopted in the *uriosometer*, employed for determining the specific gravity of urine.

The liquid to be examined by the hydrometer, is placed in a tall jar, of a diameter somewhat greater than that of the large bulb of the instrument: the temperature is then adjusted (or is carefully observed with a view to subsequent correction), and the hydrometer steadily floated in the liquid; after pressing the hydrometer down, and allowing it to regain its level, the mark to which it sinks is noted. (Since the surface of the liquid around the stem is bounded by a curve, the operator must observe that portion of the curve which has been taken in the determination of the zero, and which he can ascertain for himself, by placing the instrument in distilled water.)

The tables containing the corrections to be made for variations of temperature, often effect a saving of time, with a slight sacrifice of accuracy, since they render any adjustment of the temperature unnecessary.

DETERMINATION OF THE SPECIFIC GRAVITY OF A GAS OR VAPOR.

§ 6. The operation by which the specific gravities of gases and vapors are determined, is more complicated than those for solids and liquids, and is, in comparison with these latter, seldom called into requisition. It will therefore be necessary to give here merely an outline of the process, leaving the minute details to be acquired from experience.

The specific gravity of an aeriform substance is ascertained by comparing the weight of a certain volume, with that of an equal volume of perfectly dry and pure atmospheric air, of the same temperature and pressure.

If the substance be a gas at the ordinary temperature, the operation is executed as follows:—

A light glass globe of considerable size, fitted with a good stopcock, is carefully dried, exhausted of air, and weighed; it is then placed in connection with a system of tubes destined to purify and dry the air, which is then allowed to flow gradually in till the globe is filled: the temperature and barometric pressure having been carefully observed, the stopcock is closed, and the globe again weighed: it must afterwards be exhausted a second time, filled with the gas to be examined (in a state of perfect dryness and purity), and, the temperature and barometer having been again observed, the weight determined. If the pressure and temperature had not varied during the experiment, we have now the data for calculating the specific gravity directly, viz: the weights of equal volumes of atmospheric air and of the gas under the same conditions. If, however, the temperature or pressure exhibited a difference in the two weighings, it will be necessary to reduce both gases (by calculation) to the same temperature and pressure, before the specific gravity can be deduced.

The calculations necessary for correcting gases for temperature and pressure are given in the method of determining the density of the vapor of volatile substances, in which such calculations are most frequently necessary. (§ 8.)

DETERMINATION OF THE DENSITY OF THE VAPORS OF VOLATILE SUBSTANCES.

§ 7. A light glass globe (the diameter of which is about three inches), having a long neck about half-an-inch in diameter (which is softened in the blowpipe-flame at about two inches from the globe, and drawn out at an angle of about 100.^o to a long open point: is carefully dried, and weighed;¹ a quantity (not

¹ In very accurate experiments, the globe must be filled with dry air previously to weighing, by alternate exhaustion and readmission of air through a tube containing chloride of calcium.

less than 100 gra.) of the volatile substance, is then introduced, by warming the globe and dipping the extremity of the beak into the liquid (if a solid, liquefied by fusion); the globe is now attached to a handle or stand, and immersed, with the point projecting above the surface, in a bath of water or oil, the temperature of which must be then raised considerably higher (by 40° or 50° F.=25° or 30° C.) than the boiling point of the volatile substance. The bath should be provided with a thermometer, by which the temperature is indicated. The flame below the bath is so regulated, that the latter shall remain at a nearly constant temperature. A jet of vapor, of course, issues rapidly from the orifice of the neck of the globe; as soon as the vapor has ceased to escape (which may best be ascertained, in most cases, by applying a light), the orifice is hermetically sealed by the blowpipe, the thermometer and barometer being observed at the time of sealing (if any drops have condensed in the point of the neck, they should be chased out with a spirit-flame before sealing). The globe is removed from the bath, well cleansed, allowed to cool, and very accurately weighed. The point of the neck is now scratched with a file, and broken off under mercury, when, in consequence of the condensation of the vapor, the mercury will enter, and (unless an exceedingly volatile substance has been employed) will entirely fill the globe. If the experiment has not been very carefully performed, a bubble of air will remain in the globe. The mercury is poured from the globe into a graduated jar, and accurately measured; also, if a bubble of air was observed in the globe, the latter is again (completely) filled with mercury, and the volume ascertained. We have now the data for the determination of the specific gravity.

Fig. 3.



§ 8. In order to illustrate the method of calculating the results, let us consider an example where it was required to determine the density of the vapor of turpentine:—

Weight of the globe filled with dry air at 60° F. and 30 in. bar.	3000.304	grs.
Weight of the globe filled with vapor of turpentine at 350° F. and 29.6 in. bar. (temperature and pressure at the moment of sealing the point)	3027.474	“
Volume of mercury which entered the globe on breaking the point at 60° F. and 29.6 in. bar.	29.50	cub. in.
Volume of mercury which exactly fills the globe (i. e. capacity of the globe)	30.00	“
Difference, being the residual air (weighed with the vapor) at 60° F. and 29.6 in. bar.	0.50	“
100 cubic inches of dry air at 60° F. and 30 in. bar. weigh	31.012	grs.

From the proportion

$$100 : 30.00 :: 31.012 : x = 9.304$$

we find the weight of the (30 cub. in. of) air contained in the globe to be 9.304 grs.

Hence,

Weight of globe and air	3009.304
“ air	9.304
“ empty globe	3000.000

In order to ascertain the actual volume of vapor which was weighed in the globe, we must deduct from the total contents of the globe (30 cub. in.), the

volume of the air which had not been expelled. We find, from the above account of the experiment, that the volume of the residual air at 60° F. and 29.6 in. bar. was 0.50 cub. in. But this air was inclosed with the vapor in the globe at a temperature of 350° F., the barometric pressure being=29.6 in., and it is, therefore, necessary to ascertain what expansion it must have suffered at that temperature. This is determined by a calculation based upon the following law, which is the result of many careful observations:—

All gases expand alike for an equal increase of temperature, and this expansion amounts to $\frac{1}{480}$ of the volume which the gas would occupy at 0° F. for every degree of the Fahrenheit scale.

This law applies also to vapors when remote from their condensing points, in which case they are subject to the same laws as the permanent gases.

Now, according to this statement, 460 volumes of any gas at 0° F., would become 461 vols. at 1° F.; 460 + 2=462 vols. at 2° F., and so on. Thus the 460 vols. would have expanded to 460 + 60, or 520 vols. at 60° F., and to 460 + 350, or 810 vols. at 350° F.

$$\begin{array}{cccc} \text{Vols. at } 60^\circ & \text{Vols. at } 350^\circ & \text{Vol. at } 60^\circ & \text{Vol. at } 350^\circ \\ 520 & : & 810 & :: & 0.5 & : & x=0.78 \text{ cub. in.} \end{array}$$

Hence it appears that the air remaining in the globe would, at the time of sealing the point, occupy a volume =0.78 cub. in., which must therefore be deducted from the total contents of the globe.

$$30.00 \text{ cub. in.} - 0.78 \text{ cub. in.} = 29.22 \text{ cub. in.}$$

The volume of turpentine vapor weighed in the globe was, then, (at 350° F. and 29.6 in. bar.)=29.22 cub. in.

In order, however, to obtain the specific gravity, it is necessary to reduce this volume to the standard temperature and pressure, viz: 60° F. and 30 in. bar.

The correction for temperature is effected as in the former case, the proportion being of course reversed:—

$$\begin{array}{cccc} \text{Vols. at } 350^\circ & \text{Vols. at } 60^\circ & \text{Cub. in.} & \text{Cub. in.} \\ 810 & : & 520 & :: & 29.22 & : & x=18.76 \end{array}$$

18.76 cub. in. then, would be the volume occupied by these 29.22 cub. in. of vapor at 350° F., supposing that it would bear cooling to 60° F. without liquefaction.

A correction must also be made for the difference of atmospheric pressure, which, of course, influences the volume of the vapor. This correction is based upon the well-known law of Mariotte, that *the volume of a gas is inversely as the pressure*, which holds good also with regard to vapors removed from their points of liquefaction.

$$\begin{array}{cccc} \text{Bar.} & \text{Bar.} & \text{Cub. in.} & \text{Cub. in.} \\ 30 & : & 29.6 & :: & 18.76 & : & x=18.51 \end{array}$$

The volume, therefore, which the vapor (weighed in the globe) would have at 60° F., and 30 in. bar., is 18.51 cub. in.

What, then, was the weight of this volume of vapor? We shall ascertain this by deducting the weight of the residual air from that of the total contents of the sealed globe. The volume of the residual air at 60° F. and 29.6 in. bar. was 0.50 cub. in.:—

$$\begin{array}{cccc} \text{Bar.} & \text{Bar.} & \text{Cub. in.} & \text{Cub. in.} \\ 30 & : & 29.6 & :: & 0.50 & : & x=0.49 \end{array}$$

At 30 in. bar. then, this would occupy 0.49 cub. in., and would weigh 0.152 gr.

Weight of globe and contents (turpentine vapor and residual air)	3027.474	grs.
“ Empty globe	3000.000	“
“ Turpentine vapor and residual air	27.474	“
“ Residual air	0.152	“
Weight of 18.51 cub. in. of turpentine vapor, at 60° F. and 30 in. bar.	27.322	“
Now, 18.51 cub. in. of air, of the same temperature and pressure, weigh	5.740	grs.

$$\begin{array}{ccc} \text{Grs.} & \text{Grs.} & \\ 5.740 & : 27.322 & :: 1 : x=4.76 \end{array}$$

4.76, therefore, is the specific gravity required.

CONVERSION OF THERMOMETRIC DEGREES.

§ 9. It is very often necessary, in chemical calculations, to convert a temperature expressed in degrees of one thermometric scale into the corresponding temperature on another scale, and we may here point out the method of effecting such conversion.

The two scales commonly used in laboratories are those of Fahrenheit and Celsius, which latter is also known as the *centigrade* scale. The zero of the Fahrenheit scale is the lowest temperature produced by a mixture of ice and salt, which is 32° below the melting-point of ice, and 212° below the boiling-point of water. The centigrade scale, on the other hand, starts from the melting-point of ice (0°), and makes the boiling point of water=100°, so that 100° C. correspond to 180° F. (the number of degrees between 32° and 212°), or 10° C. to 18° F., or, to simplify it still further, 5° C.=9° F.; the calculation is now very simple, if we remember that, since the Fahrenheit scale commences 32° F. lower than that of Celsius, we must subtract 32 from all Fahrenheit degrees before reduction, and must add this number to all degrees which have been converted from the centigrade. To illustrate this by examples, let us suppose it required to find the degree upon the centigrade scale corresponding to 60° F.

$$\begin{array}{l} 60^\circ - 32^\circ = 28^\circ \\ \text{and } 9^\circ : 5^\circ :: 28^\circ : x=15^\circ.5 \end{array}$$

60° F. therefore, correspond to 15° .5 C.

Again, to find the Fahrenheit degree corresponding to 80° C.

$$\begin{array}{l} 5^\circ : 9^\circ :: 80^\circ : x=144^\circ \\ 144^\circ + 32^\circ = 176^\circ \end{array}$$

which is the temperature required. Hence, we may deduce the following rules for the conversion of thermometric degrees:—

To reduce Fahrenheit to centigrade degrees, subtract 32°, multiply by 5, and divide by 9 ($(F.-32^\circ) \cdot \frac{5}{9}$).

To reduce centigrade to Fahrenheit, multiply by 9, divide by 5, and add 32° ($\frac{9^\circ}{5} + 32^\circ$).

DEFINITION OF CHEMICAL TERMS IN CONSTANT USE.

§ 10. THERE are a few terms constantly employed in every page of chemical works, of which it is highly necessary to have a clear apprehension in the outset; we proceed to define them as generally as possible.

An ACID is a substance possessing a sour taste, the power of reddening most vegetable blues, such as litmus (acid reaction), and a tendency to combine with bases, of which it destroys, in greater or less degree, the characteristic properties. It is this total or partial annihilation of characteristic properties which is implied in the term *neutralization*, and acids are said to neutralize bases, or *vice versâ*.

Substances which do not affect test-papers are said to be *neutral*.

A *monobasic acid* is one which requires only one equivalent of a basic protoxide to form a neutral salt; whilst a *bibasic acid* requires two, and a *tribasic acid*, three equivalents of such bases.

§ 11. AN INORGANIC BASE is a metallic oxide (*i. e.* a combination of a metal with oxygen), which is capable of combining with acids, and of destroying, in greater or less degree, their characteristic properties.

An *alkali* is an inorganic base which is soluble in water; it possesses a peculiar acid taste, and is capable of restoring the blue colour to litmus which has been reddened by an acid, or of imparting a brown tint to turmeric-paper. (Alkaline reaction.)

§ 12. A SALT is a combination of an acid with a base (*oxy-acid salts*), or of a salt-radical with a metal (*haloid salts*).

This definition calls for an explanation of the term salt-radical.

A SALT-RADICAL is a substance capable of combining with hydrogen to form an acid, or with a metal to form a salt. The element chlorine is the type of this class of substances.

Sulphate of potassa, composed of sulphuric acid and potassa, may serve as an example of an oxy-acid salt; and chloride of sodium is the type of haloid salts. (*à la mer*, the sea.)

A *neutral salt* of a monobasic acid is that which contains as many equivalents of the acid as there are of oxygen in the base; the neutral salts of bibasic and tribasic acids contain respectively one-half, and one-third, as many equivalents of acid as there are of oxygen in the base. A *double salt* is a combination of two salts; thus, alum is a double salt, composed of sulphate of alumina and sulphate of potassa.

ON EQUIVALENTS.

§ 13. It is almost impossible to give any definition of the term equivalent which would not be open to exception, since there are so many opinions with regard to the conditions by which the application of the term should be regulated.

One of the neatest, and at the same time, most general definitions which can be given, is the following:—

THE EQUIVALENTS of elementary bodies (§ 68) represent the smallest proportions in which they enter into combination with each other.

The numbers representing these equivalents are, of course, referred to some standard number, taken to represent the equivalent of one of the elements. In England, the standard is hydrogen, which is made = 1; on the Continent, however, the equivalents are sometimes referred to oxygen, which is represented by 100. The two scales are distinguished as the oxygen and hydrogen scales. The equivalent of oxygen (8) upon the hydrogen-scale represents, then, according to our definition, the smallest weight of this body which is known to enter into combination with other elements. It is necessary, however, to bear in mind that this is no absolute assertion; it is not affirmed that 8 grains, or 8 parts of whatever magnitude, are the smallest absolute weight of oxygen which will enter into combination, but it is merely proposed to take 8 as representing the smallest relative quantity of oxygen which can combine with other elements; as representing, in fact, the atom of oxygen, or that quantity so small that it cannot be divided. It is on this view of the nature of equivalents that they have been sometimes called the atomic weights; but, by those who maintain the infinite divisibility of matter, they are usually termed equivalents, or combining proportions, the fitness of which latter term will be obvious.

We cannot better illustrate the meaning of the term equivalent, than by describing the method of determining that of copper.

A weighed quantity of perfectly pure black oxide of copper is heated in a stream of hydrogen gas; the latter, combining with the oxygen derived from the oxide of copper, forms water, which is converted into vapor, and metallic copper remains; this last is accurately weighed; the experiment thus conducted shows that 100 parts of the black oxide of copper contain 79.84 parts of copper, and 20.16 of oxygen, whence we ascertain, by a proportion, that 8 parts (or one equivalent) of oxygen are combined with 31.7 of copper. But we have not yet proved that 31.7 is the equivalent of copper, for the black oxide might contain more or less than one equivalent of copper for one equivalent of oxygen; and now, we must pass from experiment to hypothesis; we must assume a certain composition for this oxide, and the equivalent is then at once deduced. The black oxide of copper is generally assumed to contain single equivalents of copper and oxygen; first, because it is the more natural assumption; secondly, because it presents a striking analogy to many other oxides for which a similar composition is assumed; and lastly, because there actually exists another oxide of copper (the red oxide), which, from analogy, and from a certain tendency to decompose into metallic copper and the black oxide, is assumed to contain two equivalents of copper to one equivalent of oxygen. Upon similar principles is the determination of the equivalents of other metals effected.

The equivalent of a compound body is the sum of the equivalents of its elements.

In order to exhibit the principles upon which the determination of the equivalent of a compound body is effected, we will suppose it required to ascertain the equivalent of sulphuric acid.

For this purpose, it is necessary to analyze some pure and well-defined combination of the acid with a substance of known atomic weight. Let us suppose the sulphate of oxide of copper to be employed. It will be found to contain, for every equivalent, or 39.7 parts, of oxide of copper, 40 parts of sulphuric acid; and if we assume that this salt consists of single equivalents of acid and base, the number of 40 will represent the equivalent of sulphuric acid. The assumption proceeds here chiefly upon considerations of convenience and simplicity in the first instance; and, in subsequent cases, may, of course, be supported by analogy.

By analyzing compounds of sulphuric acid with other bases, it will be found

that either 40 parts, or some very simple multiple of this quantity, are required to form a neutral salt. Moreover, it may easily be shown that 40 parts of sulphuric acid can be replaced by 54 parts, or one equivalent, of nitric acid, and by 22 parts, or one equivalent, of carbonic acid.

It will be seen that the number 40 is the sum of one equivalent of sulphur, 16, and three equivalents of oxygen, 24.

It is highly necessary to remember that *combination takes place, whether between elements or compounds, either in the proportions of their equivalents, or in multiples of those proportions, and never in submultiples*, so that fractions of equivalents never enter into chemical notation; the law thus expressed, joined with the announcement that *individual compounds always contain exactly the same proportions of their elements*, is usually designated the *law of definite and multiple proportions*.¹

It will be evident, from what has been already said, that if we know the elements of which any compound is made up, and the number of equivalents of each element, we may at once calculate the percentage composition; and this is one of the uses to which a knowledge of equivalent numbers can be applied.

Another use of equivalents in practical chemistry depends upon the circumstance that the equivalents of elements, or compounds belonging to the same group, as regards their chemical relations (the relation of acids to acids, bases to bases, &c.), represent the proportions in which such elements or compounds replace each other in any particular combination to form another combination of the same order; for example, the equivalents of potassium and sodium (39 and 23) represent the proportions in which these elements unite with the same quantity of oxygen to form the alkalies potassa and soda, the equivalents of which (47 and 31), again, represent the proportions in which they unite with the same quantity of sulphuric acid to form the sulphates of potassa and soda; thus, by applying our knowledge of the equivalents of these alkalies, we at once ascertain how much of either of them would be required to neutralize a given quantity of sulphuric acid.

(A table of equivalents will be found at § 68.)

ATOMIC THEORY.

§ 14. We have already alluded to the existence of two views respecting the divisibility of matter; according to one of these, matter is capable of infinite division, while the other would lead us to believe that there exist certain ultimate particles, of which all matter is made up, and which are incapable of further division; these particles are termed atoms (*α priv.* and *τίμω*), and the theory based upon the hypothesis of their existence, is generally known as the *Atomic Theory of Dalton*, who was the first to propound it in a definite form.

This theory allows us to account for the various phenomena of combination and decomposition in a much more elegant and satisfactory manner than that of infinite divisibility; for if the equivalent numbers be supposed to express the relations between the weights of atoms of different substances, the law of multiple proportions follows at once; since, by the definition, fractions of these cannot enter into combination; and hence the quantities of any element existing in a series of compounds must always be multiples, by some whole number, of the equivalent weights.

The substitution of one body for another, equivalent for equivalent, is also very easily explained upon this theory.

¹ Very good examples of this are seen in the series of compounds of oxygen with nitrogen and sulphur, to which we refer.

Another necessary consequence would be the law, that the equivalent of a compound body is the sum of the equivalents of its components, for since the atoms are indivisible, the compound atom produced by their union must have their joint weight.

On this theory, the equivalent volumes of gases would actually represent the spaces occupied by their atoms.

The phenomenon of *isomerism* would also be explicable by assuming a different arrangement of the atoms of which isomeric substances are composed.

With regard to the size and shape of atoms, much discussion has taken place, but it is evident that these points (especially the latter) cannot be settled until we succeed in obtaining particles of matter so small that we cannot effect any further division; and, moreover, they are decidedly of secondary importance in a chemical point of view.

We should wish the mind of the student to be impressed with the fact, that the atomic theory is merely a collection of laws, based upon a pure assumption of the finite divisibility of matter, thus differing widely from the doctrine of equivalents, which is really the result of experiment, and the generalization of facts.

COMBINATION BY VOLUME.

§ 15. When gases enter into combination, the volumes of the combining gases always stand in a very simple ratio to each other, and if the resulting compound be also gaseous, its volume bears a simple relation to that of its components. (In most cases, a certain condensation takes place, the volume of the compound gas being less than the sum of the volumes of its constituents.) Thus, one volume of oxygen, combining with two volumes of hydrogen, produces two volumes of water in the state of gas; again, one volume of chlorine combines with one volume of hydrogen, to form two volumes of hydrochloric acid gas.

The following are two well-established laws with regard to the combination of gases by volume:—

1. *When two volumes of one gaseous element combine with one volume of another element, the resulting gas occupies two volumes.*
2. *When equal volumes of elementary gases combine, the volume of the compound gas is the sum of the volumes of its constituents.*

From what has been said with regard to equivalent weights, it follows that the proportions by volume in which the different gases combine are perfectly constant; these proportions, which, as we have already mentioned, are exceedingly simple, are usually termed the *equivalent volumes of the gases*.

This simple relation which we observe between the volumes in which elementary gases unite, is explained by the circumstance that the specific gravities of gases are either the same as their equivalents, or stand in some very simple ratio to them (of course, it is here supposed that the specific gravity and the equivalent are referred to the same standard).

CHEMICAL AFFINITY.

§ 16. CHEMICAL AFFINITY may be defined as an attraction exerted *at insensible distances*, between particles of matter of different kinds, the result of which is the formation of new particles possessed of attributes different from those of their components.

This definition at once exhibits the points of difference between chemical attraction and the forces of gravitation and cohesion.

Gravitation is exerted, *at all distances*, between masses of matter, without regard to their nature, and differs, therefore, *in toto*, from affinity.

Cohesion differs less widely from affinity, since it acts only *at very minute distances*. This force, however, is exerted more frequently, and with greater energy, between similar particles of matter than between particles of different kinds.

Moreover, the operation of these forces is not attended with any material alteration in the properties of the matter.

The fall of an apple to the earth is the result of gravitation, the force which binds the particles of the fruit together is cohesion, while the ultimate particles or elements of which the apple consists are united by chemical attraction or affinity.

The operation of chemical affinity, or combination, does not take place between substances without reference to the class to which they belong. Thus, elements are very seldom found to combine with other than elements, or quasi-elements; so rarely, in fact, do elements enter into direct combination with compound substances, that, when this is the case, it is considered to afford ground for suspecting that the element in question may hereafter prove to be a compound body. Thus, acids are never found to combine with the metals, but always with their oxides. Sulphur, chlorine, cyanogen, and the like, never combine with metallic oxides, only with metals.

The affinity of the metals for the non-metallic elements is generally much greater than their affinity for each other.

Generally speaking, the more opposite the chemical relations of bodies, the more powerful the affinity between them.

The operation of affinity is usually attended with evolution of heat; all cases of combustion are simply examples of chemical combination, attended with evolution of heat and light.

It will appear from our definition of affinity, that, since this attraction is exerted only at insensible distances, its force will be in some degree proportioned to the state of division of the masses of matter between which it is exerted; accordingly, we observe occasionally that masses which will not act upon each other, combine energetically when reduced to powder; thus, a mass of sulphur, even at a moderately high temperature, will not act upon mercury, but if they be well triturated together in a mortar, at the same temperature, combination takes place.

But this effect of mechanical division in promoting chemical attraction, is much more strikingly exemplified when the cohesion of one or more of the combining substances is diminished—*i. e.* when it is reduced to the liquid state; oxalic acid in the solid form will not act upon hydrated lime, but if a solution of oxalic acid be poured upon lime, or *vice versa*—or, above all, if they be mixed in a state of solution, immediate combination ensues, and oxalate of lime is formed.

This attractive force is not only influenced to a great extent by the state of division, but it also suffers very important modifications under various other conditions, the chief of which we shall endeavor to indicate.

The affinities of various substances for each other are modified to a very great extent by the temperature at which these affinities are exercised. Thus, hydrogen will not combine with oxygen at the ordinary temperature, but, at a somewhat elevated temperature, very energetic combination takes place. Again, to take a more complicated example, carbonate of baryta, digested at a low temperature with sulphate of soda, yields sulphate of baryta and carbonate of soda; but if these latter be boiled together, the decomposition is reversed, we obtain sulphate of soda and carbonate of baryta.

In general, however, the cause of this relation of affinity to temperature may

be traced to a difference in the state of the product or products of the action of such affinity at the different temperatures. A familiar example of this is found in the decomposition of oxide of mercury by heat, which takes place at a temperature at which both of its constituents have a tendency to assume the gaseous state, and we may suppose that this very tendency, this molecular repulsion, in fact, determines the separation of the elements. Another very striking example is seen in the action of chloride of ammonium upon carbonate of lime; if this latter be boiled with solution of chloride of ammonium, it is well known that carbonate of ammonia is formed and volatilized, whilst chloride of calcium remains in solution; whereas, if these substances (*viz.* carbonate of ammonia and chloride of calcium) be mixed in a state of solution at the ordinary temperature, carbonate of lime is precipitated, and chloride of ammonium remains in solution. The difference, in this case, appears to arise from the tendency of the particles of carbonate of ammonia to assume the gaseous form at high temperatures.

Finally, we may cite, as an important example of this modification of affinity, the decomposing action of very weak but fixed acids (*e.g.* silicic and boracic acids), at high temperatures, upon the salts of more powerful acids, which are capable of assuming the gaseous form (*e.g.* sulphuric and nitric).

The action of the force of affinity, therefore, as will be seen by the foregoing examples, is modified to a most remarkable extent, according to the cohesive force with which the particles of the resulting compound are held together; in fact, this influence of cohesion is so generally observed, when it results in the passage from the liquid to the solid state, that some authors have laid down the rule, that when any two or more solutions are mixed, the direction of the force of affinity will tend to the production of that compound which is the least soluble (*i. e.* possesses most cohesive power) under the circumstances in which it is called into existence. Examples of this form of affinity will be seen in every page of chemical works.

Light even exerts sometimes an important influence upon chemical combination and decomposition; the most familiar examples of this action are, the combination of hydrogen and chlorine, which takes place instantaneously under the influence of solar light, and the decomposition of nitric acid into peroxide of nitrogen and oxygen, which the rays of the sun are capable of inducing.

The powerful effect of electricity in modifying chemical affinity, to such an extent as to effect the decomposition of the most stable combinations, is well seen in the resolution of water into its elements (hydrogen and oxygen), by means even of a feeble galvanic current, whereas, on the other hand, the combination of hydrogen and oxygen to produce water, may likewise be induced by an electric spark passed through the mixture of the gases.

Certain solid substances possess a most remarkable power of inducing combination; this is especially the case with metals, and above all, with platinum, which may be obtained by particular processes, in the forms of platinum-sponge and platinum-black, these being simply platinum in a state of minute division: if either of these be introduced into a mixture of oxygen and hydrogen gases, in the proportions in which they combine to form water, the metal becomes at once redhot, and the combination takes place with explosion. This action is generally referred to a specific power, possessed by the platinum, of condensing the gases within the minute pores upon its surface, and of thus bringing them within the sphere of mutual attraction; but why this power should reside especially with the metal in question, has not been fully explained.

The affinities possessed by a substance in its *nascent* state, *i. e.* at the moment of its elimination from a compound, are often much more energetic than under ordinary circumstances.

This is especially noticed in the powerful oxidizing action of mixtures capable of yielding oxygen; *e.g.* of binoxide of manganese and sulphuric acid; and in

the increased affinity for oxygen which is possessed by nascent hydrogen, as evolved by the action of zinc upon liquids containing free sulphuric or hydrochloric acid.

Other circumstances might be adduced, which are capable of altering the direction of this force; but the above comprise the chief modifying agencies to which chemical attraction is subjected in practice, and the others will be more advantageously studied in individual examples.

Enough, we trust, has been said, to show that affinity is subject to so many modifications that its results can be predicted only to a very limited extent; and, therefore, that it is preferable for the student of chemistry to acquire a knowledge of the laws of the action of this force from experience of its effects, rather than to rest any faith in such general laws and tables of affinity as were popular among the chemists of a former day, and which, though they might be faithful guides in some cases, left almost as much to unlearn, in exceptions, as they taught in rules.

CHEMICAL DECOMPOSITION.

§ 17. The causes which induce chemical decomposition may be conveniently considered under two divisions: the first, comprising those cases of decomposition which do not take place in consequence of an opposition of affinities, and which are therefore purely phenomena of decomposition unattended by recombination; and the second division embracing such decompositions as result from the affinity of the decomposing agent, or of one of its constituents, for some constituent of the body which is decomposed.

The decompositions belonging to the first class are chiefly those effected by the physical agents, heat, light, and electricity. The power of heat to induce decomposition has already been noticed in one very simple example (that of oxide of mercury; see Affinity); but this action of heat is so universally and readily available, that it is constantly applied in the laboratory; its results are so varied that it is scarcely possible (and we know not whether it would be useful) to classify them, but we may remark that they consist very seldom in the separation of the ultimate elements of any compound, but usually in the production of certain combinations which are more volatile or more stable than the original material. When organic substances are decomposed by the action of heat alone, they are usually said to be subjected to *destructive distillation*, and are resolved into compounds much less complex (*i. e.* containing a smaller number of equivalents) than the substance from which they originated.

Electricity is an important agent of decomposition, and has somewhat recently received a very interesting application in certain researches upon organic substances. Decompositions by electricity are usually effected by means of the galvanic battery, and their results may, to a great extent, be predicted. It does not come within the scope of this elementary work to give a complete history of the *electro-chemical theory*, as that system of laws is termed according to which the results of the action of electric currents can be determined by *a priori* considerations; but the leading principles of this theory are of sufficient importance to call for a passing notice.

It is found that when bodies are decomposed by a galvanic current (or, as it is termed, subjected to *electrolysis*) one of the constituents is invariably disengaged at the wire in connection with the positive pole of the battery, and the other at the negative pole; to take an example which has been already alluded to, the decomposition of water by the galvanic current, we find that the hydrogen is always disengaged at the negative, and the oxygen as invariably at the positive end of the battery. Now, it will be remembered that bodies in a like

electric state do not attract each other, but only those which are in a dissimilar condition; hence, since hydrogen is attracted by the negative pole of the battery, and oxygen by the positive, it follows that hydrogen is, with respect to oxygen, an electro-positive element, and *vice versa*; in the same manner, it is found that the metals are disengaged at the negative pole of the battery, and the non-metallic bodies with which they are in combination, at the positive; or, if the salts or oxygen-acids be operated upon, that the bases are eliminated at the negative, and the acids at the positive pole.

Agreeably to this distinction, all the elements and some compounds are arranged in two series, the members of which are respectively positive and negative in relation to each other.

The chief features of the electro-chemical theory, therefore, are, that the class of electro-positive substances (or those which are disengaged at the negative end of the battery) comprehends hydrogen, the metals, and their basic oxides, whilst oxygen, chlorine, and most of the non-metallic elements, together with the acids, are the chief members of the other class. It must, however, be borne in mind, that this distinction is only relative, and that one substance may be electro-positive to a second, and negative to a third body; thus sulphur is electro-negative with respect to silver, and electro-positive in relation to chlorine (which stands higher on the electro-negative scale than sulphur).

The decomposing influence of light may be traced in its action upon the salts of silver, upon nitric acid, &c.

In some cases, decomposition may result from a mere mechanical shock, as in the case of certain detonating compounds, which explode when lightly touched; in these cases, it would seem that the affinity between the elements is so slight, that the least external disturbance is sufficient to upset the equilibrium.

It will immediately occur to the mind of the more advanced student, that there are some decompositions effected by causes which are yet unknown; of this description are fermentation and the so-called effects of catalysis (decomposition by contact) concerning which no decisive result has at present been arrived at.

True chemical decomposition, resulting from the operation of affinity, may take place in a variety of ways.

The simplest case is that in which a substance seizes one constituent of a compound for which it has, under existing circumstances, a greater affinity than the other constituents have; this case is often termed one of *simple elective decomposition*. Examples of this form of decomposition are seen in the reduction of certain metallic oxides by hydrogen, or carbon, at high temperatures, and in the evolution of carbonic acid by the action of stronger acids upon the carbonates.

Another case is that which is popularly termed *double elective decomposition*, wherein two substances act simultaneously upon a third, each appropriating one of the constituents of this third body. The formation of the chlorides of boron and silicon, by the simultaneous action of chlorine and carbon upon boracic and silicic acids, are cases in point.

Double decomposition is said to take place when an interchange of constituents is effected between two compounds; as when sulphate of potassa and nitrate of baryta yield sulphate of baryta and nitrate of potassa.

CHEMICAL NOMENCLATURE.

§ 18. Before proceeding to the study of individual chemical compounds, we must acquaint ourselves with the methods adopted in order to render the name of a substance in some way expressive of its constitution.

The combinations of all simple electro-negative substances (and even of com-

pounds resembling them in their chemical relations) with metals or non-metallic bodies, are generally distinguished by the termination *ide*. Thus we have oxides, chlorides, sulphides, cyanides, &c.

When these compounds contain single equivalents of their elements, they are often distinguished by the prefix *proto*. Thus, the terms protoxide, protochloride, &c., indicate compounds of single equivalents of the metal or non-metallic substance, with oxygen, chlorine, &c. In the following pages, however, we have preferred to omit this prefix, and to designate all such compounds by the simple names, oxide, chloride, &c., since all compounds containing more than one equivalent of either constituent are distinguished by their appropriate prefixes.

In order to express a compound of this description containing more than one equivalent of the electro-negative constituent, we make use of the prefixes *bi*, *ter*, *penta*, *sesqui*, &c.; thus, the compound of two equivalents of chlorine with one equivalent of tin is termed the bichloride of tin; that of three equivalents of oxygen with two equivalents of iron (*i. e.* of $1\frac{1}{2}$ equivalents with one equivalent), the sesquioxide of iron, &c. Where there are more than one equivalent of the electro-positive constituent combined with one equivalent of the electro-negative, the prefix *sub* is employed; the compound of two equivalents of mercury with one equivalent of chlorine is known as the subchloride of mercury, and so forth.

The prefix *per* is usually employed to designate that combination of a metal with an electro-negative body which contains the greatest quantity of the latter, except in the case of oxides, where it is applied to the highest oxide which does not possess acid properties.

Acids derive their name from their characteristic element. In the case of hydrogen-acids, the name of this element is simply coupled with an abbreviation for hydrogen, as in the case of hydrochloric acid, hydrosulphuric acid, &c. Oxygen-acids of the same element are distinguished, according to the amount of oxygen which they contain, by particular prefixes and terminations. The chief acid of the series terminates in *ic*, and is without a prefix; this is the case with sulphuric, phosphoric, arsenic, nitric acids, &c. The acid which ranks next to this generally terminates in *ous* without prefix, as phosphorous acid, arsenious acid, &c.; but where an intermediate acid has been discovered after these names were established, its name, in general, terminates in *ic*, and is distinguished by the prefix *hypo*, indicating that it contains less oxygen than the principal acid; an example of this is hyposulphuric acid. An acid containing more oxygen than the chief acid is known by the prefix *hyper*, as hyperchloric acid, which contains more oxygen than chloric acid.

In the same way, acids in *ous* containing less oxygen than the chief acid in *ous*, are distinguished by the prefix *hypo*; hyposulphurous and hypophosphorous acids will serve as illustrations.

Salts receive names which indicate both the acid and the base of which they are composed. Salts formed by acids in *ic* are distinguished by the termination *ate*; the terms sulphate and phosphate imply the salts of sulphuric and phosphoric acids; when the acid terminates in *ous*, the salts receive *ite*; the sulphites and phosphites are the salts of sulphurous and phosphorous acids. If the acid have a prefix, it is of course retained in the name of the salt.

In naming a salt of the oxide of any metal, the word oxide is usually omitted, for the sake of brevity; thus, sulphate of copper should strictly be sulphate of oxide of copper, and the word oxide must always be understood in naming salts of oxygen acids. Salts formed by the combination of acids with suboxides are usually known by the prefix *sub*; thus, subsulphate of copper implies the sulphate of suboxide of copper. In the same way, the salts of peroxides and sesquioxides are usually distinguished by the prefixes *per* and *sesqui*.

Salts which contain more acid than is requisite to form a neutral salt with the

amount of base present, are termed *acid salts*, whilst those in which the base predominates are designated *basic*. If the amount of acid be twice as great as is necessary to form a neutral salt, the compound is distinguished by the prefix *bi*, as bisulphate of potassa ($\text{KO.SO}_3, \text{HO.SO}_3$), bitartrate of potassa (KO.HO.T).

Combinations of water with other compounds are termed *hydrates*.

Substances which are not combined with water are said to be *anhydrous*.

Compounds possessing the same composition, but differing in their chemical properties, are said to be *isomeric*; or, if the compounds in question are similarly constituted, as regards the proportion of their elements, but differ in the actual number of equivalents which they contain, they are termed *polymeric*.¹

CHEMICAL NOTATION.

§ 19. In order to exhibit, concisely and distinctly, the manner in which substances act upon each other, giving rise to new forms of combination, chemists make use of certain universal symbols and formulæ, which, when connected by particular signs, are made to represent all possible combinations. We shall proceed to elucidate some of the most important principles of this valuable system of notation.

Each element is represented by its own symbol, which is sometimes the initial letter, sometimes the characteristic letters taken from the English or Latin designation of the element, and this symbol represents one equivalent of such element; thus, N represents one equivalent of nitrogen, Na (*natrium*) one equivalent of sodium, Fe (*ferrum*) one equivalent of iron, &c.

When more than one equivalent of an element is to be expressed, it is effected by placing a small figure beneath and to the right of the symbol; thus, two equivalents of nitrogen are represented by N_2 , four equivalents of sulphur by S_4 , &c.

In order to indicate a combination of two or more elements, the symbols representing such elements are simply arranged side by side; sulphuric acid, a compound of one equivalent of sulphur and three equivalents of oxygen, is represented by SO_3 ; starch, containing twelve equivalents of carbon, ten equivalents of hydrogen, and ten equivalents of oxygen, is written $\text{C}_{12}\text{H}_{10}\text{O}_{10}$.

Some compounds, however, are denoted by particular symbols; thus, cyanogen (C_2N) is usually represented by Cy, tartaric acid ($\text{C}_6\text{H}_4\text{O}_{10}$) by $\bar{\text{T}}$, oxalic acid (C_2O_2) by $\bar{\text{O}}$, &c. In the last two cases, of organic acids, the electro-negative mark (-) is used as the sign of acidity. Organic bases, in like manner, are distinguished by the electro-positive sign (+).

In writing a combination of two or more compounds, they are usually separated by points or commas; thus, the formula of sulphate of alumina, composed of alumina (Al_2O_3) and sulphuric acid (SO_3) is written $\text{Al}_2\text{O}_3.3\text{SO}_3$; and alum, containing sulphate of alumina, sulphate of potassa, and water, is expressed by the formula $\text{KO.SO}_3, \text{Al}_2\text{O}_3.3\text{SO}_3 + 24\text{HO}$.

To express more than one equivalent of a compound, the elements of which are not separated by a point, a large figure is simply placed to the left of the compound, as in the example of sulphate of alumina; but when the elements are separated by a point, the compound must be inclosed in a parenthesis, and the coefficient must be placed outside and to the left; thus, two equivalents of sulphate of alumina are expressed by $2(\text{Al}_2\text{O}_3.3\text{SO}_3)$.

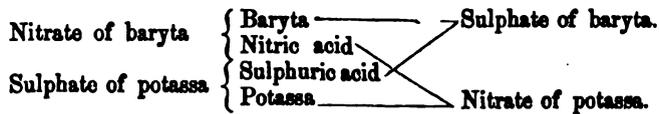
¹ Urea ($\text{C}_2\text{H}_4\text{N}_2\text{O}_2$) is isomeric with cyanate of ammonia ($\text{NH}_4\text{O.C}_2\text{NO}$) and the oil of spiræa (hydride of salicylic acid $\text{C}_{14}\text{H}_8\text{O}_4$, H) with hydrated benzoic acid ($\text{C}_{14}\text{H}_8\text{O}_3$, HO). On the other hand, cyanic acid ($\text{C}_2\text{N}_2\text{O}$), fulminic acid ($\text{C}_4\text{N}_2\text{O}_2$), and cyanuric acid ($\text{C}_6\text{N}_4\text{O}_3$) are polymeric compounds.

The sign + generally indicates either a state of mixture merely, or a lower order of combination; the expression $\text{KO.SO}_3 + \text{BaO.NO}_3$ implies that sulphate of potassa is mixed with nitrate of baryta. The water contained in alum exists in a more loosely combined state than the sulphuric acid and alumina.

The sign of equation = is used to imply that the elements or compounds placed before such sign would give rise to those which follow it; thus, in the case of sulphate of potassa and nitrate of baryta, sulphate of baryta and nitrate of potassa would be produced, and the reaction (as it is termed) would be expressed by the *equation*



In complicated reactions, greater simplicity is often attained by means of diagrams, in which the rearrangement of the various elements is indicated by lines; thus, to represent the preceding reaction in a diagram:—



(A list of symbols will be found at § 68.)

PHENOMENA RELATING TO THE PHYSICAL CONDITION OF BODIES.

THE fundamental principles of chemical philosophy having been explained, there still remain to be considered, before entering upon the special study of chemical operations, certain phenomena relating rather to the physical condition of bodies, an acquaintance with which will be found necessary to the proper comprehension of their chemical history.

SOLUTION.

§ 20. SOLUTION consists in the diffusion of one substance (whether solid, liquid, or gaseous) through a liquid, in such a manner as to produce a homogeneous mass. This may be the effect either of true chemical combination or of mechanical mixture.

When solution depends upon the formation of a chemical compound, heat is generally evolved; whilst if it be a purely mechanical process, either no change of temperature takes place, or a depression is observed.

In the solution of hydrate of potassa (fused potassa) in water, a considerable amount of heat is disengaged, since the hydrate combines with the water; whereas nitrate of potassa, when dissolved in water, gives rise to a considerable fall of temperature.

When a solution has taken up as much of the dissolved body as it is capable of doing, the solution is said to be *saturated*.

Generally speaking, heat promotes the solution of solids and retards that of gases; but some solids are less soluble at high temperatures; this is the case with lime, and with sulphate of soda.

If a hot solution contains more of the dissolved body than, when cold, it would be capable of retaining, the excess of the dissolved body will be deposited as the solution cools; and, if it be a solid, generally in the form of *crystals*, which are larger and more distinct, the more slowly they have been deposited.

Whenever a separation of a solid body from a solution takes place, it is termed *precipitation*, and the solid which separates is called a *precipitate*.

CRYSTALLIZATION.

§ 21. CRYSTALLIZATION is the spontaneous arrangement of the particles of solid bodies in regular geometric forms.

A tendency to such an arrangement is generally observed in solids which are gradually deposited from a state of solution, but sometimes in those which have condensed into the solid from the gaseous form, or in masses solidified after fusion.

When the particles of a solid substance are not arranged in regular geometric forms, it is said to be *amorphous*; when it crystallizes in two distinct forms, which cannot be referred to the same primitive form, it is termed *dimorphous*.

If two substances are found to be capable of crystallizing in the same geometric form, or in forms which may be referred to the same primitive, they are designated *isomorphous*—a term also applied to substances which, though themselves incapable of crystallizing, are found to replace each other in particular combinations without materially altering their crystalline form. This last sense of the term *isomorphous*, is that in which it is most frequently received, and may be illustrated by the three alkalies, potassa, soda, and oxide of ammonium, which replace each other in the class of salts known as the alums, without altering the crystalline form of the latter. The alums are double salts, composed of an alkaline sulphate and a sulphate of some basic sesquioxide, combined with a large amount of water of crystallization; the alums have all the same crystalline form. The observation of this isomorphism is often useful in enabling us to decide upon the atomic constitution of certain compounds.

FORMS OF CRYSTALS, &c.—We enter upon the subject of crystallography with some considerable hesitation, as it is not within the province of this work to discuss any subject belonging strictly to physics; and, moreover, as crystallography may at the present day be regarded as forming of itself an important branch of natural science. Since, however, it is usual, and frequently of very great importance, to pay some attention to the physical structure of the various solid compounds with which the chemist meets, both in nature and in his laboratory—since he is thereby frequently enabled to discriminate, with the greatest nicety and rapidity, between different substances, or, at any rate, to read therein something concerning their nature which may aid him considerably in his subsequent researches; and, as we shall also repeatedly make use of certain crystallographical terms in the description of elements and their compounds, we propose to give as brief and general an outline of this subject as we imagine will meet the wants of the student.

Most solid substances have a certain characteristic form in which they crystallize; this form is, however, not always peculiar to themselves, since many substances, widely different in their chemical character, crystallize in forms similar to each other. We have already made mention of a property possessed by some substances of crystallizing in two distinct forms. Examples of *dimorphous bodies* are carbon and sulphur.

If a smart blow be applied to a cube of rock-salt, or a prism of calcareous spar, and the smallest fragments resulting from the fracture of the two crystals examined, they will be found to be identical in form with the original masses. (The tendency possessed by crystalline forms to split in certain directions is termed their *cleavage*.) All crystals are therefore built up of small particles possessing a regular form, either identical with that of the crystal itself, or standing in some simple relation to it. We are not only enabled to reduce a crystal, by cleavage, to smaller forms, as already described, but it is also possible, by attending to certain precautions (§ 55), to add to the size of a crystal, without in any way altering its form. These facts, added to certain optical properties possessed by many crystals, prove that crystalline bodies possess a certain regular structure.

All crystalline forms exhibit *faces* or *planes*; *edges*, or lines of contact of two planes, and *points* or *angles*, which are formed by the meeting of three or more planes.

An imaginary line drawn from one angle to an opposite one, passing from side to side, or from end to end, through the centre of a crystal, is called its *axis*. The particles of a crystal may therefore be conceived to be symmetrically arranged round an axis of this description. A slight consideration will show that various crystals may possess a different numbers of axes, which have different lengths, and cross each other at different angles.

When a crystal is examined as to its form, it is held in such a manner that one of the axes is situated vertically in front of the observer's eye; if the axis

of a crystal vary in length, the *longest* is chosen for this *vertical axis*; if they are equal, any one may be chosen. The axis thus placed, is called the *principal axis*, while the others are called *secondary*.

All crystalline forms may, according to the nature of their axes, be arranged in *six systems*. These systems embrace what are called the *primary forms* of crystals, from which the *secondary forms* are produced. The meaning of the latter term may be explained in a few words.

If a crystal be allowed to grow in such a manner that each plane, angle, and edge is equally increased, it is self-evident that, however large the crystal becomes, its form will remain the same. If, however, from some cause, only one portion of the crystal be added to (if, for example, a crystal be not regularly turned about, as directed at § 55), the form of the crystal will undergo a change. Now, if this alteration of the form of a crystal be effected in a certain regular manner, new figures will result, which will stand in a direct geometrical relation to the form of crystal from which they were produced. Such forms are called *secondary forms*, belonging, of course, to the same system as their original or *primary form*. It is evident that a great variety of forms may be produced in this way, by the systematic removal, to a greater or less extent, of angles, edges, and planes.

We will now confine ourselves to a brief description of the principal forms belonging to the six different systems, generally accepted in crystallography.

I. The *regular system* includes those crystals which have three equal axes, at *right angles* with each other.

The principal forms of this system are:—

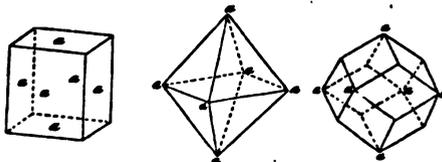
4. The *cube*, which is inclosed by six equal square planes.
5. The *regular octohedron*, inclosed by eight equilateral triangles.
6. The *rhombic dodecahedron*, inclosed by twelve equal rhombic planes.

In the figures, the directions of the three axes are shown by the letters *a—a*.

Fig. 4.

Fig. 5.

Fig. 6.



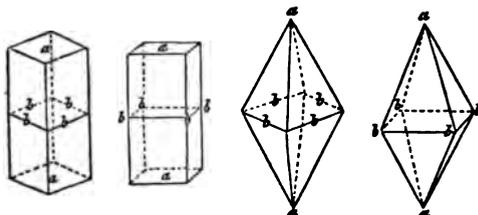
II. The *square prismatic system*. The crystals of this system also have three axes, which are at right angles with each other; one of these, however—the *vertical axis*—is either longer or shorter than the other two. Of this system, the principal forms are:—

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.



a—a principal axis. *b—b* secondary axes.

7. The *right square prism*, of which the secondary axes terminate in the centres of the lateral planes.

8. The *right square prism*, of which the secondary axes terminate at the edges of the lateral planes.

9. The *right square-based octohedron*, of which the directions of the axes correspond to those of prism 7.

10. A *similar octohedron*, of which, however the directions of the axes correspond to those of prism 8.

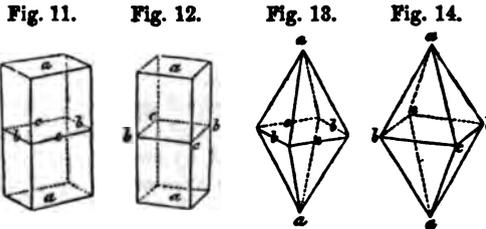
III. The crystals belonging to the *right prismatic system*, have, like those of the former systems, three axes at right angles to each other; they are, however, all of unequal lengths. This will be observed in the following forms of this system:—

11. The *right rectangular prism*, with the secondary axes terminating in the centres of the lateral planes.

12. The *right rhombic prism*, of which the secondary axes terminate at the edges of the lateral planes.

13. The *rectangular-based octohedron*, with axes corresponding to those of prism 11.

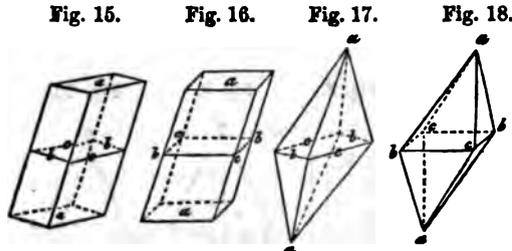
14. The *right rhombic-based octohedron*, with the axes corresponding to those of prism 12.



a—a principal axis. b—b, c—c, secondary axes.

IV. The crystals of the *oblique prismatic system* have, like the foregoing, three axes, but they are no longer all at right angles. The two secondary axes of these are at right angles, but the principal axis is perpendicular to one of these, and oblique to the other. This system is represented by the following forms, of which the axes stand in the same relation to each other as those of the forms given of the former system:—

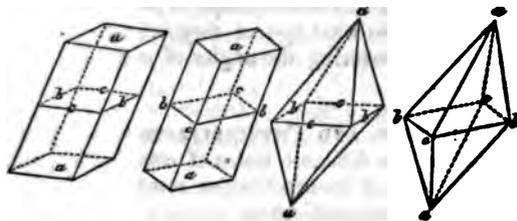
15, the *oblique rectangular prism*; 16, the *oblique rhombic prism*; 17, the *oblique rectangular-based octohedron*; 18, the *oblique rhombic-based octohedron*.



a—a principal axis. b—b, c—c, secondary axes.

V. In the crystals of this, which may be called the *doubly-oblique prismatic system*, all the three axes are oblique to each other. This system is represented in the figure, by two prisms, 19 and 20, and two octohedra, 21 and 22.

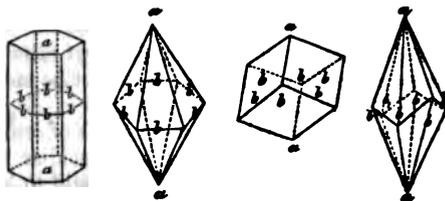
Fig. 19. Fig. 20. Fig. 21. Fig. 22.



a—a principal axis. b—b, c—c, secondary axes.

VI. The *rhombohedral system*. The forms of this system differ considerably from those of the foregoing, by containing *four axes*, instead of three. Of these four, the vertical or principal axis is perpendicular to the other three, which lie all in the same plane, are equal, and inclined to each other at an angle of 60° . The examples here given of the forms belonging to this system are: 23, the *regular six-sided prism*; 25, the *rhombohedron*; 24 and 26, two species of *dodecahedron*.

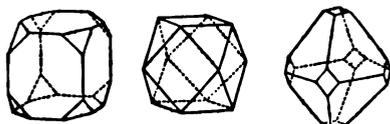
Fig. 23. Fig. 24. Fig. 25. Fig. 26.



a—a principal axis. b—b secondary axes.

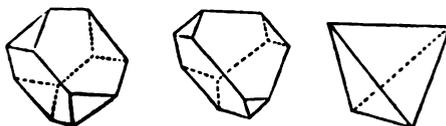
It has been already explained how the so-called secondary forms may be derived from primary forms; the following figure, showing the passage of the cube to the octohedron may serve to render this point more intelligible.

Fig. 27. Fig. 28. Fig. 29.



There is one other important class of crystals that demands some slight explanation, this is the *hemihedral class*. If the alternate planes or faces of a crystal be allowed to grow excessively, it will be found that the other planes gradually become diminished, and at length they are perfectly obliterated, a new form of crystal being the result. This kind of action is shown in the conversion of the *octohedron* into the *tetrahedron*.

Fig. 30. Fig. 31. Fig. 32.



The foregoing statements will at once convince the student of the great importance of possessing some means of submitting crystals to an accurate measurement, in order to ascertain to what system they belong. Several instruments have been constructed for measuring the angles of crystals; they have received the name of *goniometers*.

WATER OF CONSTITUTION AND CRYSTALLIZATION.—Crystalline salts frequently contain water in two different states of combination, which are distinguished by the terms *water of constitution* (or sometimes *basic water*, or *water of hydration*), and *water of crystallization*.

The water of crystallization is much less intimately combined with the salt than the water of constitution, and is therefore more easily expelled.

In order to exhibit this difference, the water of hydration is usually expressed by its chemical formula (HO), and is incorporated in the formula of the salt; whilst the water of crystallization is represented by the mechanical symbol (Aq), and is connected with the formula by the sign +, as will be seen in the examples given below.

The reason for applying the term water of crystallization to that portion of the combined water which is most easily expelled, is found in the influence which it exerts upon the crystallization of the salt. Most salts containing water of crystallization lose their crystalline form upon its expulsion, and crumble to an amorphous powder.

This water of crystallization is retained by different salts with very different degrees of force, but rare are the cases where it cannot be entirely expelled at a temperature of 212° F. (100° C.)

Many salts lose this water by simple exposure to air of ordinary dryness; and as the escape of the water is usually attended by a peculiar opaque appearance assumed by the surface of the crystals, such salts are said to be *efflorescent*. The ordinary phosphate of soda ($2\text{NaO.HO.PO}_5 + 24\text{Aq}$) and the sulphate of soda ($\text{NaO.SO}_3 + 10\text{Aq}$) are familiar examples of such salts.

Other salts effloresce only in perfectly dry air, or *in vacuo*, as will be more fully explained in the section upon desiccation.

Those salts which do not effloresce at ordinary temperatures, generally do so when exposed to a moderate degree of heat, and in most cases lose the whole of their water of crystallization at 212° F. (100° C.); this loss of water is frequently attended with an alteration in the color as well as in the form of the salt; the well-known blue crystals of sulphate of copper (blue vitriol, $\text{CuO.SO}_3 + 4\text{Aq}$) for example, crumble down to a nearly white powder when heated in the water-bath, the four equivalents of water of crystallization being thus eliminated.

A salt is sometimes met with in crystals of different form, containing different quantities of water of crystallization.

Thus, ordinary borax (biborate of soda, $\text{NaO.2BO}_3 + 10\text{Aq}$) crystallizes in six-sided prisms, containing, as indicated by the formula, ten equivalents of water of crystallization, whilst octohedral borax contains but five equivalents.

Again, the common phosphate of soda (2NaO.HO.PO_5) crystallizes in two different forms, containing respectively 14 and 24Aq, whilst two forms of the sulphate of soda are known with 8 and 10 equivalents of water.

When heat is applied to salts containing water of crystallization, they sometimes dissolve in this water, undergoing, as it is termed, the *aqueous fusion*; when the water of crystallization has been expelled, they generally become solid again, and undergo the *true* or *igneous fusion* when the temperature is still further increased. The behavior of phosphate of soda ($2\text{NaO.HO.PO}_5 + 24\text{Aq}$), when heated, affords a good example of this.

Crystals destitute of water of crystallization, do not, of course, undergo the

aqueous fusion; when such crystals (as, for example, chloride of sodium, NaCl , nitrate of potassa, KO.NO_3) are heated, the water mechanically inclosed within them is converted into vapor, which, in its endeavor to escape, splits the crystal asunder, producing a cracking sound, which has gained for this phenomenon the name of *decrepitation*.

The water of constitution contained in salts is, as already mentioned, not so easily expelled as the water of crystallization, and cannot generally be separated without some alteration in the chemical nature of the salt, whence this form of combined water has received its present designation. The alteration in the nature of the salt sometimes amounts merely to a diminution of solubility, sometimes to a true chemical decomposition and production of a new compound.

The green crystals of sulphate of iron (green vitriol) have the composition $\text{FeO.SO}_3.\text{HO}+6\text{Aq}$; if these are heated to 212°F . the 6 Aq are expelled, and the salt falls to a nearly white powder; but if the crystals are heated to redness, the whole of the water is expelled, and FeO.SO_3 , almost insoluble in water, remains. Again, if the crystals of phosphate of soda ($2\text{NaO.HO.PO}_3+24\text{Aq}$) are heated to redness, they lose their twenty-five equivalents of water, and become 2NaO.PO_3 , a totally different salt from the former, and called pyrophosphate of soda. (The constitutional water, in this instance, should strictly be called basic water.)

The water of constitution may also sometimes be replaced by some neutral salt, thus giving rise to the production of a double salt; for instance, in the sulphate of iron ($\text{FeO.SO}_3.\text{HO}+6\text{Aq}$), the one equivalent of water of constitution may be replaced by sulphate of potassa (KO.SO_3), and the formula of the double sulphate of potassa and oxide of iron is $\text{FeO.SO}_3.\text{KO.SO}_3+6\text{Aq}$.

DIFFUSION OF GASES.

§ 22. The diffusive power of gases is the tendency which they possess to intermix, even through very small apertures, and in opposition to the force of gravitation. Thus, if two bottles be filled, the one with hydrogen, the other with carbonic acid gas, which is many times heavier, and be connected by means of a glass tube, however narrow, and arranged even so that the heavier gas must rise if it mix with the lighter, we find that, after a few hours, the two gases will be contained in both bottles in the same proportions. The rate of diffusion of a gas represents the velocity with which it passes through very minute apertures, as compared with the rate of passage of some other standard gas through apertures of the same size.

This diffusion of gases takes place through all porous bodies (*e. g.* dry membrane, plaster of Paris, dry cork, unglazed earthenware), and through the smallest crevices; so that gases should never be kept for any length of time in cracked vessels, or in jars closed with plain corks.

Gases differ very considerably in their rates of diffusion, which vary inversely as the square roots of the densities (specific gravities) of the gases. Thus, the densities of hydrogen and oxygen are to each other as 1 : 16; the square roots of these numbers are respectively 1 and 4; the rates of diffusion will therefore be as 4 (for hydrogen) : 1 (for oxygen).

The superior diffusive power of hydrogen over air may be well illustrated by means of Graham's *diffusion tube*, which consists of

Fig. 83.



a glass tube (Fig. 88), about half an inch in diameter and twelve inches long, closed at one end with a plate of plaster of Paris, of about one-sixth of an inch in thickness; if this tube be perfectly dried, filled with hydrogen, and its open extremity immersed in water, the gas will diffuse through the pores of the plaster so much more rapidly than air will enter, that the water may be seen to rise in the tube to the height of several inches.

This law of diffusion appears to afford an explanation of the uniform composition of atmospheric air, and of the non-accumulation of injurious impurities in the atmosphere.

CHEMICAL MANIPULATION.

APPARATUS NECESSARY FOR THE PREPARATION OF GASES.

THE conditions for the evolution of gases are various. Some are evolved at common temperatures, while others require various degrees of heat to effect their disengagement. The form of apparatus employed for their preparation varies considerably in consequence.

APPARATUS FOR THE DISENGAGEMENT OF GASES WITH THE AID OF HEAT.

§ 23. Iron bottles, such as those in which mercury is imported, having a piece of iron pipe about two feet in length firmly screwed into the opening, are generally used when the temperature required to disengage a gas amounts to a red heat, as in the preparation of oxygen from binoxide of manganese. The most convenient mode of conducting the gas disengaged in this apparatus to its reservoir, is by fixing a piece of wide glass tube into the end of the iron pipe, by means of a cork, in the manner to be presently described, and tying upon this a piece of vulcanized Indian-rubber tubing of sufficient length.

Gases which are obtained by distillation are conveniently prepared in tubulated glass retorts; the form of apparatus being, in fact, almost the same as that employed in ordinary distillation, to be described under that head; the retort is connected, in the ordinary manner, with such purifying or collecting apparatus as circumstances may require.

The apparatus most generally in use for the preparation, on a moderate scale, of gases requiring heat for their disengagement, consists of flasks of various descriptions, appropriately fitted with corks, bent tubing, and caoutchouc connectors, to the purifying and collecting apparatus.

It will be necessary to enter a little into detail respecting the various portions of this kind of apparatus, and the mode of constructing it.

FLASKS.—Various forms of flasks are used as gas-generators, but those most commonly employed are the Florence oil or wine flasks, and the thin flat-bottomed German flasks, the necks of which latter terminate in a thick rim of glass. The principal advantage of the former is their cheapness; in many cases the oil-flasks are far too small; the wine-flasks (which are not so frequently met with) are generally very narrow in the neck, which is a serious obstacle to their use in cases where it is necessary to introduce a safety or funnel-tube in addition to the conducting-tube.

In selecting Florence flasks for use, particular attention should be paid to the following precautions: that they be thin at the bottom, and as uniform in substance as possible; that they contain no air-bubbles of any considerable size;

and that the necks be wide, tolerably uniform in bore throughout, and stout at their orifices.¹ It is advisable to fuse the sharp edges of the mouths of these flasks, by very gradually heating them in the blowpipe-flame.

The flat-bottomed Florence flasks are of but little use in the disengagement of gases, as they are generally very thick at the bottom, and consequently unable to stand any sudden change of temperature.

In selecting the flat-bottomed *hard glass flasks*, the above precautions should likewise be attended to; the necks of these should not, however, be chosen too wide, as they frequently exceed those of the Florence flasks so much in width as to render it difficult to fit them properly with corks.

CORKS.—The conducting-funnel and safety-tubes are fitted into the flasks by means of corks. Since, in the preparation of gases, it is of the utmost importance that the apparatus should be perfectly tight, great care must be bestowed upon the choice of proper corks. They should be compact, and at the same time, elastic; or such as will admit of being rendered so by pressure, without splitting.

TUBING.—In selecting tubing for the various connecting portions of an apparatus of this description, care should be taken that its diameter be such as to admit of the introduction of the requisite number of tubes into the cork, at a proper distance from each other, and that the thickness of the glass is in such proportion to its diameter, that it may be bent in a proper manner, and possess sufficient strength to resist the amount of pressure applied in introducing it into the corks.

SAFETY-TUBES are essential portions of all apparatus for generation of gases.

Fig. 34.



The most simple form of safety-tube consists of a long piece of tubing introduced through the cork, into the flask or generating vessel, so that the lower extremity may be covered to about an inch by the liquid contained therein, and protruding above the flask to the height of from one to three feet, or even higher, according to the pressure to which the liquid in the vessel is liable to be subjected by the generation of the gas.

The length of such tubes is sometimes very inconvenient; in which case, however, they may be advantageously replaced by *Welter's safety-tube* (Fig. 34), in which a small quantity of mercury or other liquid is made to act as a valve. It is inserted into the cork of the flask or vessel, so as to protrude into the latter about half an inch. The funnel-tube, to be presently described, also acts, simultaneously, as a safety-tube.

When but little or no liquid is used in the preparation of a gas, the operator may substitute for the above safety-tube, a piece of tubing of about five or six inches in length, passing a little way through the cork into the generating vessel, and closed at the other extremity by means of a small caoutchouc cap, or plug of cork, which is easily forced off when the pressure becomes excessive, or may be removed by the operator, if absorption takes place.

FUNNEL-TUBES should be selected of sufficient length to be introduced so far into the generating vessel as to be covered by the liquid inside to the extent of about half an inch, and to protrude some distance beyond the cork, as above mentioned.

§ 24. METHOD OF FITTING UP APPARATUS FOR THE GENERATION OF GASES.—It now becomes necessary to give some description of the manner in which an apparatus of this kind should be constructed; the directions will be

¹ A good method of removing the oil from Florence flasks is to boil a strong solution of common carbonate of soda in them for some time, and afterwards to wash them repeatedly in water.

given in general terms, so as to be applicable to the fitting up of any apparatus consisting of glass vessels, tubes, and corks.

OPERATIONS WITH THE CORKS.—In fitting a cork to a vessel, it should be first softened, either by pressure between the fingers, or, if large, by rolling it under the foot, or by gentle hammering. In order that the apparatus may be tight, it is necessary that the cork thus softened should require a gentle pressure for its insertion, and be slightly conical. In case it is somewhat too large for insertion, its size may be reduced either by cutting with a very sharp knife, or by filing a portion off by means of a fine rasp. Great care must, however, be taken in these operations, that the conical form of the cork be perfectly preserved, or it will be impossible to make it fit tightly. In fitting a cork into a flask, tube, or bottle, these must invariably be held close to the aperture; as otherwise, should the pressure applied in introducing the cork be so great as to break the glass, the most serious consequences to the operator may result. It is, indeed, always most prudent to hold the glass apparatus in a cloth during this operation.

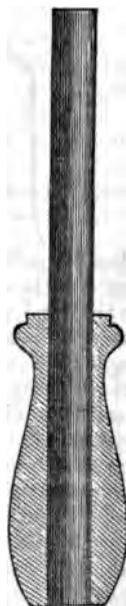
Perforations must next be made in the corks, for the introduction of the necessary tubes. The cork is pierced in the proper place, by means of a small *rat-tail file*, care being taken to bore it straight through; the size of the hole may be then increased to any extent by filing, and substituting a larger file as the aperture increases.

In order to obtain a perforation of equal bore throughout, it is necessary to introduce the file alternately at the opposite ends of the cork. A very convenient implement for making these perforations is the *cork-borer* (Fig. 35), particularly when large holes are required; great care must, however, be taken in boring them, to maintain the borer in a perfectly straight direction. When the cork is very thick, it is advisable to bore half through on the one side, and then to draw out the borer and complete the perforation in the proper place from the other side. Should the perforation required not correspond in size to any of the cork-borers at hand, the next size smaller should be chosen, and the perforation afterwards increased to the proper dimensions by means of a rat-tail file. When more than one perforation has to be made in a cork, care must be taken that the holes be perfectly parallel, and that a partition of cork of sufficient thickness be left between them; likewise, that the perforations are not made too close to the side of the cork. If these precautions are not attended to, the cork is easily torn and rendered unfit for use on inserting the tube, or on fitting it into the vessel.

§ 25. **OPERATIONS WITH TUBING.**—A piece of tubing of proper bore and diameter having been selected for use, the first operation to be performed with it, is that of cutting it into lengths for the various portions of the apparatus. To this end, a deep mark is made in the glass, by means of a sharp three-edged file, at the spot where the tube is to be divided, and it may then be broken with a jerk. Should the tube be rather large and thick, it becomes necessary to continue the file-mark completely round the glass. It is very difficult to cut off large tubes smoothly with the file alone; sometimes the file-mark may be continued into a crack with a redhot iron, and led round the tube. Another plan is to clasp the tube (where it is marked) with an iron wire, bent into the form of a hook, and heated to bright redness. If the hot glass be then moistened with water, a crack is produced, which may be afterwards led round the tube.

The tube thus cut into lengths, now requires to be bent in order to receive the proper form for the necessary conducting tubes. For all ordinary gas-appa-

Fig. 35.



ratus, the tube has to be bent at right angles; but for syringe-bottles, small tube-apparatus, &c., it requires bending at more or less acute angles; the mode of manipulating is, however, in all cases the same.

For ordinary, and even for tolerably hard glass tubing, provided it be not very large or thick, a simple spirit-lamp, or bat's-wing gas-jet, may be used as the source of heat. The tube is supported on each side of the portion to be heated, and held over the flame for a short time, being turned round continually, in order that it may become uniformly heated, and also moved slightly backwards and forwards so as to heat a sufficient surface. When the tube has become thoroughly heated, it is introduced into the upper portion of the flame, and continually moved about as before until it is soft to the touch, and has been uniformly heated to the length of about an inch, or even more, if a very round bend is required; by a gradual pressure, the requisite inclination is then given. The principal precautions to be observed in bending tubes, are: not to have the

Fig. 36.

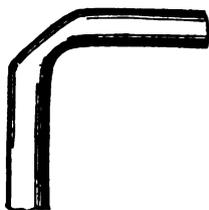
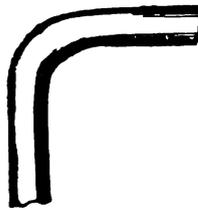


Fig. 37.



glass too soft, and to heat it uniformly, or the bend may become distorted and flattened at the convex portion (Fig. 36); to give no other than a downward direction to the hand, so that the two extremities of the tube remain in corresponding directions; to heat a sufficient length of the tube, so that the bend may not be at a sharp angle, but round (Fig. 37); to apply only a very slight pressure in bending, otherwise, as soon as the tube becomes too cool to yield, it will snap. If a very round bend is required, one portion of the glass must be bent first as far as admissible, without affecting the bore of the tube or distorting it; the neighboring portions are then heated, and the bend continued in the same manner until the requisite curve is attained. Very thin tubes must always be bent very round, or else the convex portion of the bend is certain to become flattened, and so thin as to be very fragile when cool, and the concave portion will bend in folds, and become otherwise distorted. If gas is at hand, the ordinary fish-tail burner affords a most convenient flame for making round bends, as a large surface of tube may be heated by it at one time. Unless the tube has been heated too powerfully, no difficulty will be found in removing, when cool, any carbon that may have been deposited upon it by the gas. Should the tube to be bent be of larger dimensions, and consist of glass not easily fusible, the table or the Herapath mouth-blowpipe must be employed for heating it, the same precautions being observed as above directed.¹

Before introducing tubes into the corks, it is necessary to round the sharp edges of the extremities of the former, which would otherwise cut and injure the

¹ Should the bend required be so near one extremity of the tube as to preclude the possibility of supporting the short end with the fingers, or should it be even at the very extremity, the force necessary on this side must be applied by pressing against the glass with an iron rod; the latter should, however, not be applied until the moment that the curvature is to be made, nor retained in contact with the glass so long as to reduce its temperature below the point of softness, as there would be great risk of cracking the glass under those circumstances.

perforations prepared for their reception. This is effected by fusing the extremities, either in the flame of an ordinary lamp or by the blowpipe. This operation requires considerable care, on account of the great facility with which tubes crack at the extremities. It is necessary first to heat the tube gradually, as directed above, to the extent of about an inch from the termination, and to remove it slowly from the flame until the extreme end only remains therein. As soon as the edge becomes faintly redhot, the tube should be entirely removed, as otherwise it will contract at the extremity, which is sometimes very inconvenient. After having heated a tube, the operator must be careful to avoid placing the heated portion upon any cold surface, such as the table, until it has cooled down considerably. The force applied in pushing the tube into the cork must be very gradual and gentle; the best plan is to screw it in; it is also advisable, when the tubes fit rather tightly in the perforations, or when the former are rather large, to grease them slightly at the extremity first introduced.

When the tubes are properly inserted, the cork is fitted into the vessel with great care; it being held firmly between the thumb and two first fingers, and screwed round, a gradual downward pressure being simultaneously applied.

The cork having been thus pressed into the vessel as far as possible, it is requisite to ascertain whether the fitting is air-tight. Should the cork contain more than one tube, it is necessary, in order to do so, to close the exterior openings of all but one. The mouth is then applied to the open tube, a portion of the air sucked out of the vessel, and the tongue immediately placed against the opening. If the apparatus is tight, the tongue will be forced into the aperture. Or, instead of sucking out the air, an extra portion may be forced into the vessel from the mouth, and the tongue then pressed against the opening to prevent its escaping from that quarter. If there be any leakage in the vessel, the air will be heard to issue from the place at which the leakage exists, and the pressure against the tongue will gradually diminish. By the latter test, the precise spot at which the apparatus is defective may be easily ascertained.

It is always preferable, if possible, to fit up an apparatus perfectly air-tight with good corks alone; should this, however, not be practicable (which is frequently the case when the corks are large, or the openings of the vessels not perfectly round), recourse must be had to luting.

§ 26. LUTES.—Various substances may be employed as luting to corks. The most convenient are, almond-paste, linseed-meal (or a mixture of both), white-lead, and plaster of Paris. If the leakage of a cork be but slight, and in the substance of the cork itself, it may be stopped by the application of a solution of sealingwax in spirits of wine, which penetrates into and fills up the small pores. But if the leakage be found to exist at any point where the cork touches the glass, it is advisable to cover the whole cork with one of the lutes above mentioned. The compactness and adhesiveness of linseed and almond lute is much increased by the addition of a little alkali to the water with which the meal is mixed. It is also advantageous to dissolve a small portion of glue in the water employed in making plaster of Paris luting.

If the gas to be generated may be at once collected, without undergoing any purification, the apparatus generally consists of a flask containing, tightly fitted, by means of a cork, a funnel or safety-tube, and a delivery-tube, which last is either bent twice downwards (the short end, which fits into the cork, at a right angle, and the long end at a more or less obtuse angle); or it is bent once, in the form of the siphon, the bend being a very round one, and the short arm fixed into the cork.

If the gas is to be collected over a pneumatic trough, the long end of the tube is bent upwards at the extremity, at an angle of about 65°. The same form of tube may be used if the gas is to be collected in gas-holders; but it will be

found far more convenient to shorten the delivery-tube, and attach it to a piece of vulcanized Indian-rubber tubing of sufficient length.

Very frequently, the gases require purification previously to collection or use; in that case, the long arm of the delivery-tube is likewise bent at right angles, and connected with such purifying apparatus as will be presently described.

If only a small quantity of gas requiring heat for its disengagement is to be prepared, much saving of time and material is effected by the use of a test-tube, or very small flask, in the place of the larger flask, into which is fitted, by means of a perforated cork, the short arm of a tube bent in the form of a siphon, the extremity of the long arm being bent upwards, as described above. This little apparatus may be conveniently held over a spirit-lamp by means of a test-tube holder, and requires no safety-tube, as it may be removed from the water into which the delivery-pipe dips, the moment the evolution of gas ceases.

APPARATUS FOR THE GENERATION OF GASES AT ORDINARY TEMPERATURES.

§ 27. When no application of heat is necessary to aid the evolution of a gas, two different forms of vessels may be employed as generators, namely, the *Woulfe's bottle*, and corked wide-mouthed bottles.

THE Woulfe's BOTTLE.—This very convenient piece of apparatus consists of a bottle with two or three separate openings, which may be fitted with corks of the ordinary size. It presents a great advantage over common glass bottles, as two or three tubes may be fitted into it perfectly air-tight, with great ease. When required for generating gas, it need only have two openings, one for the funnel or safety-tube, and the other for the delivery-tube. Great care should be taken that the interior of the necks of these bottles be perfectly cylindrical. When Woulfe's bottles cannot be obtained, wide-mouthed bottles may be substituted, provided they can be fitted with good bungs, to which tubes may be adapted in the manner before directed. The principal difficulty attending their use, is that of fitting them air-tight, since large corks can be but rarely obtained free from flaws, or sufficiently elastic to allow of proper softening. It is therefore almost always necessary in their use to have recourse to luting.

ARRANGEMENTS FOR PURIFYING GASES.

§ 28. It is frequently necessary to subject the gases to purification previously to collecting them, in order to remove trifling admixtures of other gases, or particles of liquids which are frequently held in mechanical suspension. This is effected, either by allowing the gas to pass through liquids of various descriptions, or over solids; the former being contained in common or in Woulfe's bottles, properly fitted up with connecting-tubes, &c.; the latter, in tubes of various forms.

If a Woulfe's bottle with three necks is employed, the centre neck is fitted with a safety-tube, passing nearly to the bottom of the vessel; into the neck on the one side is fitted a tube bent at right angles, and reaching likewise nearly to the bottom of the vessel, while the third neck also contains a tube bent at right angles, but protruding into the vessel only about half an inch beyond the cork. With the latter tube is connected (in a manner to be presently described) either another purifying vessel, or the delivery-tube. Should the Woulfe's bottle only have two necks, it is advisable to fit into one a piece of tube sufficiently wide to admit conveniently the delivery-tube of the generator. This wide tube should reach to within about half an inch of the bottom, and be cut off obliquely, or slightly notched at the lower extremity. This not only acts as a safety-tube, but also presents a movable joint, which is very convenient, since the gene-

rating apparatus may be turned about, or detached from the remainder, with great ease.

Fig. 38.

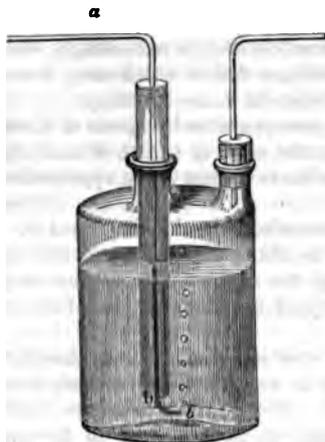


Fig. 39.



In the absence of Woulfe's bottles, such wide-mouthed bottles as have been described already may be fitted up in a similar manner, and answer the purpose very well, provided the fittings are perfectly tight.

CONNECTION BY MEANS OF CAOUTCHOUC JOINTS.—The bottles just described, having been properly charged with the purifying agent (with which they should not be more than half filled), are connected with the generating apparatus (and with each other, if more than one be required) by means of caoutchouc connecting-pieces. These little tubes, which are indispensable to every gas-apparatus, since they impart to it the necessary flexibility to permit of the individual portions being moved about and disconnected from the remainder with ease, are very easily made of sheet caoutchouc, about the tenth or twelfth of an inch thick, in the following manner: A piece of this caoutchouc of the required length is gently warmed, so as to render it perfectly flexible and soft; it is then put round a piece of glass tubing or rod, not quite the size of the intended connector. The portions that project on either side are pressed together so as to adhere pretty closely; they are then cut off with a very sharp pair of scissors. The two edges are thus obtained perfectly clean, and adhering slightly to each other; they are now pressed closely together, care being taken not to soil the cut edges. When this operation is neatly and properly performed, the two fresh surfaces join accurately together, and provided they are perfectly clean, they will adhere to each other so firmly, that the tube will tear quite as easily at any other place as at the junction. It will frequently happen that the connector will adhere so firmly to the glass on which it is made, as to render it extremely difficult to remove it without fracture. The application of a small quantity of flour, or other fine powder, to the inner surface of the caoutchouc will prevent this; or should this have been neglected, a drop of water, held to the one extremity of the tube, will be immediately sucked in between it and the glass, when it may then be removed with great ease. Should there be any slight defect in the connector, it is well to make a

Fig. 40.



second one upon it, the joint of which should be made on the opposite side to that of the inner one; the two tubes may be made to join at the extremities, by clipping a small quantity off; this must not be done at one cut, as the tube would then be closed at the ends, but the scissors should move round the tube.

Small pieces of vulcanized Indian rubber tubing, which is now made of almost any dimensions, answer the purpose of these connectors exceedingly well; they may not adhere to the glass quite so tightly, a defect which may, however, be remedied, by tying them firmly upon the tubes at each extremity.

In connecting the various portions of a gas-apparatus by means of these joints, the ends of the glass tubes should be about the sixth or eighth of an inch distant from each other, inside the connector, in order to impart to the apparatus a proper degree of flexibility.

The tying of these joints upon the glass tubes, should they need it, requires some care. The best material for tying is silken cord, of moderate thickness. The force employed in tightening and tying the cord round the connector should be very moderate; as, otherwise, the safety of the inclosed glass tube is endangered.

It is sometimes necessary to pass gases over solids of different descriptions, in the state of lumps or powder. These solids are contained in straight tubes, or in tubes bent in the form of the letter U. The straight tubes are employed of various diameters (from $\frac{3}{4}$ to $\frac{1}{4}$ inch) and lengths, according to the substance they are to contain, and are fitted at each extremity with a good cork, containing a piece of narrow glass tubing about two inches in length, and protruding about one-eighth of an inch through the cork; these serve to connect them, with the aid of caoutchouc joints, to any form of apparatus. It is advisable to place against the inner extremity of each narrow tube a small piece of cotton-wool or asbestos, in order to prevent any particles of the solid in the tube from being carried out by the current of gas. If the solid is in powder, the tube should not be filled too full, in order that a small passage may be formed between the upper part of the latter and the powder, by knocking the tube lengthwise upon the table.

Should the solid used be in the state of lumps, they should be of moderate size, smaller fragments being introduced alternately with larger, in order that no large space may be left in the tube.

If it is necessary to weigh these tubes, it is better to cut the corks off even with the tube, and to coat them with sealingwax, to prevent their absorbing moisture, and thus altering the weight of the apparatus.

The U-tubes are only employed for solids in the state of lumps, and are filled and fitted up in the same manner as the straight tubes, excepting that the narrow tubes which are fitted into the corks are not straight, but bent at right angles.

APPARATUS FOR COLLECTING GASES.

§ 29. Gases are, with few exceptions, collected over water, unless the dry gas be required, when mercury is employed in its stead.

When a gas is prepared in any considerable quantity, or it is wished to preserve it for any length of time, it is collected in gasometers, or gas-holders.

The former have been almost entirely superseded in the laboratory by the Pepys's gas-holder; we shall, therefore, confine ourselves to a brief description of the latter.

THE GAS-HOLDER.—This apparatus consists of a closed cylindrical vessel, usually of copper, which is surmounted by a circular, shallow trough of the same diameter, resting upon four pillars. Into the centre of the bottom of the trough is fixed a pipe, which passes through the top of the gas-vessel, and reaches nearly to the bottom.

Another pipe is introduced into the bottom of the trough, near to the side, which also passes into the top of the gas-vessel, where it terminates. Both these pipes may be opened or closed at pleasure, by means of stopcocks placed between the trough and the gas-chamber. Another stopcock is fixed into the side of the latter, as close as possible to the top, and a short, wide pipe is fixed obliquely into the side of the chamber near the bottom, in such a manner that the upper edge of the pipe inside shall be situated about half an inch lower than the lowest edge of the outer extremity. This pipe is closed by means of a screw-plug. In addition to this, the gas-chamber is provided with a glass gauge, which serves to indicate the amount of its gaseous contents.

The gas-holder is filled with water by closing the pipe at the bottom, opening the three cocks, and then pouring water into the trough. After the lateral cock has been closed, the last traces of air are allowed to escape through the water in the tray. The other stopcocks are then closed, and if the vessel be perfectly tight, the water will not flow out upon removal of the plug. This vessel is filled with gas by introducing the delivery-tube of the apparatus into the pipe at the bottom; the bubbles of gas, as they issue from it, will displace the water. The gas-holder should be so placed that the water may flow into a tub as it is expelled. When the gas-bubbles issue from the pipe, the holder is quite full; the delivery-tube is then removed, and the pipe closed by means of the screw-plug. The lateral stopcock is used to pass the gas through a jet, or any other form of apparatus.

In cases where a greater pressure of water may be required to force the gas through any apparatus, a long tube-funnel is screwed into the opening of the central pipe in the trough, and kept full of water, which subjects the gas in the chamber to considerable pressure.

Great care should be taken to keep the trough filled with water, and to disturb, the moment it takes place, the rotary motion frequently acquired by the water when it descends rapidly through the pipe, in order to prevent the gas becoming mixed with air, which is carried down with the water in considerable quantity, directly the above motion is set up. A piece of wood placed in the water will prevent this occurring, by being drawn to the centre the moment-rotation takes place.

In order to collect gas in a jar from such a gas-holder, it is filled with water, and placed over the shorter tube in the tray; the longer tube is then opened, so that the water may exert some pressure upon the gas, which is thus forced up through the shorter tube into the jar.

GAS-BAGS AND BLADDERS.—It is frequently necessary to receive the gas in bladders or bags. These are generally filled, as above described, from the gas-holder. The size of the bladders required is very various. When the opening of a bladder is softened by means of warm water, it may be easily fitted upon a brass cap, which may be screwed to a stopcock. It is necessary always to soak bladders in warm water before use, in order to soften them, and thus to facilitate the removal of the whole of the air from them. Gas-bags are now generally made of water-proof Indian-rubber material, the seams being rendered perfectly air-tight by means of caoutchouc.

When gases are prepared in smaller quantities, they are collected in glass vessels of various descriptions, over water or mercury, contained in vessels called pneumatic troughs.

THE PNEUMATIC TROUGH is a vessel, generally of copper or iron, of such dimensions that large jars may be moved about and filled with water in it; various supports and shelves are fixed, or made so as to slide backwards and forwards below the surface of the water, upon which the gas-receivers may be placed. If the gas is soluble in water, it is necessary to collect it over mercury, in a vessel called

THE MERCURIAL TROUGH, which is similar in construction to the water-trough, but very much smaller, on account of the great weight and expense of mercury. It is usually made of Berlin porcelain, cast-iron, or wood. When manipulating with a mercurial trough, it is always necessary that the latter should stand in a tray, and the mercury should not be allowed to remain in the trough when not in use, but be poured back into its bottle through a strainer.

The vessels used for collecting gases for experiments are of various forms. The principal are gas-cylinders, stoppered gas-jars, capped jars, and wide-mouthed bottles. When the quantity of gas to be operated upon is but very small, it is most conveniently collected in test-tubes.

GAS-CYLINDERS should be about twelve inches in height, two to four inches in diameter, of moderate thickness, and ground at the edges, so as to admit of being closed by a plate of ground glass.

TUBES of various sizes, plain, or graduated, are frequently employed in pneumatic experiments (particularly in the analysis of gases). These tubes should be of a bore sufficiently narrow to enable the operator to close their orifice with the thumb.

STOPPERED GAS-JARS are useful of various sizes. They should not be too narrow in proportion to their height; they are provided with openings at the top, into which glass stoppers are accurately ground. These jars may also be very tightly closed by means of good corks.

CAPPED JARS are of the same description as the foregoing, the opening being fitted with a brass cap, into which a stopcock may be screwed. These jars are particularly convenient for transferring gases.

STOPPERED BOTTLES of various sizes, are frequently employed for collecting gases and preserving them for some time.¹ Great care should be taken that the stoppers of these bottles fit accurately. In order to prevent their becoming fixed in the bottles, it is advisable to grease them slightly with tallow or pomatum. The same precaution should be adopted in the case of stoppered gas-jars.

There are various methods for *loosening stoppers* when they become fixed in bottles or jars. The most simple is that of tapping the stopper on each side alternately with the handle of a file or chisel, the iron portion of the tool being held closely in the hand. Should they not be loosened by this means, a gentle heat may be applied to the neck for a few moments and the tapping repeated. An excellent plan consists in fitting a wooden lever (furnished with holes of different sizes) on to the stopper, and exerting a gradual force until it is loosened.

In some cases, particularly if the bottle contain liquids, it is advantageous to heat the neck by friction instead of by flame, to accomplish which a piece of stout cord is passed once round the neck, and drawn to and fro.

If the stopper has been fixed in a bottle by the crystallization of any substance, it may frequently be removed by placing a drop or two of a solvent round the edge of the stopper, and allowing it to remain for a day or so.

§ 30. One or two precautions are necessary in the preparation and collection of gases. It is advisable that they should not be generated too rapidly, as, when purification is necessary, much of the gas evolved may escape the action of the purifier; and there is also danger, when the gas is evolved with effervescence, of the liquid in the generator rising so high as to pass over through the conducting-tube into the gas-holder, or any other portion of the apparatus with which it may be

¹ Stoppered bottles filled with any gas which it is wished to preserve therein for some time, should be placed in an inverted position, with their necks immersed in water. A strip of stout vulcanized Indian-rubber fixed tightly across the open mouth of the bottle before it is filled, and moved to one side when the stopper is being introduced, may be afterwards slipped across the top of the latter, upon which it strains with sufficient force to prevent the stopper being loosened by a slight accidental blow, or by a slight expansion of the gas within the bottle.

connected. The addition of an acid for the disengagement of a gas should, therefore, be always gradual, particularly in cases where the chemical action is accompanied by the disengagement of much heat. When the application of heat is necessary for the disengagement of a gas, it should always be applied gradually, and only raised as the evolution of gas diminishes in rapidity. When gases are prepared in flasks or retorts, these are supported by the ring of a retort-stand, or by a tripod-stand, over the gas-burner or lamp by which they are heated. It is advisable, particularly when the vessel contains a liquid, to place between it and the ring or stand, a small copper or iron tray (or *sand-bath*), similar in form to a shallow scale-pan, and filled about one-half with dry sand of moderate fineness. The retort or flask is pressed down into the sand, so as to be well covered with it. This contrivance serves greatly to regulate the heat, and render its application uniform over the whole surface of the bottom. A square piece of moderately fine wire gauze, slightly depressed in the centre, for the better reception of the flask or retort, may also be employed, particularly if the gas is disengaged merely from a solid substance. Great care should be taken not to allow the sides of the vessel to become too hot, as portions of liquid, converted into vapor by the heat, will frequently condense in the cool part of the neck, or upon the cork, and trickle down the sides of the vessel, which, if too hot, would immediately crack upon coming in contact with the cooler liquid.

Before proceeding to the collection of a gas, it is first necessary to ascertain whether, and to what extent, the gas is soluble in water. If its solubility be trifling, cold water may be employed, and warm or hot water if the gas be more soluble. The mercurial trough is used if the gas to be collected is exceedingly soluble in water, or if it is wished to obtain the gas perfectly dry. Tubes or cylinders are generally employed for collecting gases over mercury. In filling these with mercury, they should be held in a sloping position, and the liquid metal poured in very gradually. The retention of air within the tube or cylinder, by its adhesion to the glass surface, should be avoided as much as possible. The best method of accurately filling the vessel, is to pour the mercury in through a small funnel, into the neck of which is fitted a long glass tube of narrow bore, reaching to within a quarter of an inch of the bottom of the vessel. By this method the risk of fracture of the latter by the weight of the falling mercury is avoided, and the retention of air prevented by the slow and regular advance of the column of metal up the sides of the vessel. In inverting its opening over the trough, the tube or cylinder must be firmly grasped with the one hand, while the other is employed in retaining the mercury in the vessel, the mouth of which, if sufficiently small, is closed with the thumb, or if not, with a cushion of caoutchouc.

Before collecting a gas, the portions evolved during the first two or three minutes should be allowed to escape, since they are contaminated with the air contained in the apparatus. In accurate experiments, a small portion of the gas should be collected in a tube, and a test of its purity applied, before it is suffered to pass into the vessel prepared for its reception.

§ 31. Some gases which are soluble in water, and which have a corrosive action upon mercury (*e. g.* chlorine), require to be collected by displacement, as it is termed (*i. e.* in vessels filled with air, which they are made to displace). This method is also frequently adopted when mercury is not at hand, and it is necessary to collect a gas in the dry state. Wide-mouthed stoppered bottles, or gas-cylinders, are employed for collecting gases by displacement; the mode of passing the gas into the receiver varies according to its density. With *gases heavier than air*, the delivery-tube, in connection with the generating apparatus, is made of sufficient length to pass down to the bottom of the bottle or cylinder. The first portions of the gas, as they issue from the apparatus, will diffuse themselves with more or less rapidity through the air in the receiver; after a time, however,

the atmospheric air becomes almost perfectly expelled. The current of gas passing into the receiver should be as rapid as possible; it is also advisable to close the mouth of the latter partially, by means of a glass plate, to guard against the diffusion of the gas into the external air. When it is believed that the receiver is filled with the gas as perfectly as possible,¹ the delivery-tube should be disconnected from the apparatus, and gradually taken out with one hand, while with the other hand the operator should hold, close to the mouth of the vessel, the stopper or glass plate, with which the former is closed the instant the extremity of the tube is withdrawn.

If the gas be lighter than air, the bottle or cylinder in which it is to be collected must be fixed in an inverted position over the extremity of the delivery-tube, which is of sufficient length to pass up to the bottom of the vessel. The mouth of the receiver should be partially closed, by means of a piece of cardboard, or a loosely fitting cork, through which the tube passes. When the bottle or cylinder is properly charged, it is slowly raised till above the opening of the delivery-tube, when the cardboard or cork is rapidly removed, and replaced by the stopper or glass-plate, the vessel being maintained in the inverted position until its mouth is properly closed.

§ 32. COMBUSTION OF GASES.—It is frequently necessary to burn a gas as it is disengaged. For this purpose, the delivery-tube of the apparatus is replaced by a jet, which is generally made of glass tubing. A piece of narrow tube of hard glass is heated in the manner described previously, at such a distance from the one extremity as to enable the manipulator to hold the shorter end with the fingers during the operation. When the heated portion of the tube has become soft, it is drawn out. The short end is then separated from the longer one by means of a sharp file, at about the centre of the portion drawn out, and the elongated extremity of the latter is fused at the edges, by being held for a short time in the flame of a spirit-lamp.

On applying a light to the gas issuing from the jet, it will inflame and burn steadily, provided the evolution of gas be regular, and not too rapid. It is always necessary to allow the gas to escape into the air for two or three minutes, before applying a flame to the jet, in order that all the atmospheric air may be expelled; unless this be strictly attended to, the most serious consequences may result, explosive mixtures being formed by most inflammable gases with the oxygen of the atmosphere. It is also advisable, even after having waited some time, to envelop the principal portion of the apparatus in a cloth, before applying a light to the jet. If a combustible or explosive gas is to be ignited, it should be collected in stout glass vessels, and the precaution should always be taken, to wrap the vessel in a cloth, previously to setting fire to the gas; it should also invariably be firmly held by the hand, or otherwise fixed, in order that the concussion produced by the combustion or explosion may not overturn the vessel.

DETONATION OF GASES—The power possessed by the electric spark of inducing the combination of gases, has been applied with great success in analytical experiments.

It is not our intention to enter into any minute details respecting *eudiometry* (as this method of analysis is termed), but to confine ourselves to a brief descrip-

¹ The period when the vessel is properly charged with gas, may be ascertained with sufficient accuracy for ordinary purposes, either by the intensity of color of the gas in the receiver (as with chlorine), or by ascertaining whether the gas is issuing from the mouth of the vessel in a sufficiently pure state to exhibit strikingly any one of its chemical properties. Thus, in collecting carbonic acid by displacement, when the vessel is considered charged, a lighted taper should be held near its side, a little below the opening whence the air is expelled. If the receiver is properly filled, the taper will be instantly extinguished by the carbonic acid as it streams over down the side of the vessel.

tion of the manner in which the detonation of gases is effected, and the apparatus employed for the purpose. Gases are generally detonated over mercury, the explosion being effected in an instrument termed an *eudiometer*.

EUDIOMETERS.—There are two kinds of eudiometers in general use. The ordinary straight eudiometer is a graduated glass tube, of about half an inch to an inch in diameter, near the closed end of which are inserted, while the glass is soft, two pieces of moderately-stout platinum wire, at opposite sides, in such a manner that their extremities inside the tube approach each other within a convenient distance for the passage of the electric spark. To one of the wires is attached a small metal chain, passing to the ground, or fixed at the other extremity to the outside of the Leyden jar.

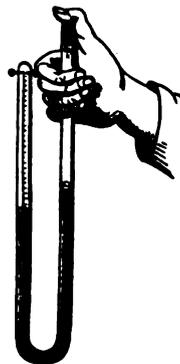
When this eudiometer has been charged with the gas to be detonated, it is held firmly in the hand, or secured by a heavy support, the open end below the mercury being pressed down with some force upon a cushion of caoutchouc, and the detonation is then effected by approaching the charged jar or disk to the outer extremity of one of the wires. It is well to wipe the glass in the vicinity of the wires with a warm, dry cloth, before passing the spark. Two persons are generally required to perform the operation; the one to hold the tube firmly, the other to detonate. When the gas has been detonated, the pressure exerted upon the caoutchouc cushion must be very gradually diminished, in order to permit the mercury to enter the tube gently (to fill up the vacuum left by the explosion). The amount of gas introduced into a tube for detonation must vary according to the amount of expansion attending the explosion. The eudiometer should never be more than two-thirds filled with gas.

Ure's *siphon eudiometer* consists of a tube with wires inserted as above, but which is bent in the form of the letter U; the open limb being somewhat longer than the other. The gas having been introduced into the closed limb, a portion of the mercury is removed from the open end by means of a small pipette, so as to equalize the mercury in the two limbs. The open limb is then firmly grasped, and the opening closed with the thumb; one of the wires may then be approached to the charged electrophorus-disk, and the gas inflamed, the spark being conducted away by the thumb, which touches the other wire. If the charge be given from a jar, this wire must be connected with the chain attached to the outside of the jar.

§ 33. COMBUSTION IN GASES.—Substances are generally introduced into gases, for combustion, by means of small metal (*deflagrating*) spoons, fixed to a piece of iron wire, which passes at the other extremity through a small metal disk, provided in its centre with a cork or stuffing-box. When the spoon is introduced into a bell-jar or wide bottle, the disk falls upon the opening from which the stopper has been removed, and prevents the escape of gas, unless there be much pressure from inside in consequence of the formation of vapors, when the disk will be forced up.¹

The wire with the spoon attached should never reach lower in the vessel than two-thirds of its depth. Some substances (steel watch-springs, &c.) may be

Fig. 41.



¹ In the combustion of phosphorus in oxygen, care should be taken that the former be perfectly dry before introduction. A small piece of phosphorus should be used for the experiment, and the gas should be contained in a large jar. When substances incombustible under ordinary circumstances are to be burnt in oxygen (such as watch-springs and metal wires), their lower end should be heated and dipped in sulphur, or a piece of German tinder, wood, or cork, should be attached to it. These are inflamed immediately before the wire or watch-spring is introduced into the gas.

attached to a simple wire by means of thread, or of very fine iron-wire, and thus lowered into the vessel. Before projecting a powder into a gas, the stopper of the vessel containing the latter should be first replaced by a glass plate, and the powder introduced gradually, care being taken to prevent any of it from falling against the sides of the vessel, as the heat disengaged by its combustion will, in such cases, frequently crack the glass. A small quantity of water should be left at the bottom of the vessel.

§ 34. TRANSFERENCE OF GASES.—It is frequently necessary to transfer gases from one vessel to another. The manner in which a gas is transferred from a gas-holder to another vessel, has been already described. Bell-glasses, which cannot, like bottles, be closed at the openings through which the gas was admitted, are transferred, when filled, from the pneumatic trough to the table, upon a common plate or saucer, in which sufficient water is retained to cover the mouth of the jar. The depth of the plate or saucer need be but very slight, as the smallest quantity of water surrounding the mouth of the jar is sufficient to prevent the gas from escaping. Gas-cylinders are transferred from the trough by closing the mouth with a ground-glass plate.

In transferring a gas from one jar to another, the jar into which the gas is decanted is filled with water, and placed, inverted, upon the shelf of the trough, so that only about one-third of its edge rests thereupon; the jar containing the

gas to be transferred is then depressed into the trough by the right hand, and so inclined that the gas may pass up into the first-mentioned jar. Much care is required in transferring gases from large into small jars or bottles. It is advisable, in these cases, to introduce the beak of a funnel, inverted under the water, into the vessel to be filled, in order that the gas, as it escapes in great bubbles from the large jar, may ascend more easily into the smaller opening of the vessel to be filled, by which means the risk of loss will be much lessened. When the vessels

containing the gases are larger than those which are to receive them, it is also very advantageous to transfer the gas first into a lipped vessel, and from thence into the smaller vessel, as the former, of whatever dimensions it may be, only delivers small bubbles of gas from the lip.

§ 35. MEASUREMENT OF GASES.—The apparatus necessary for measuring gases are, the pneumatic or mercurial trough, graduated jars and tubes, plumb-lines, supports, a thermometer, and a barometer.

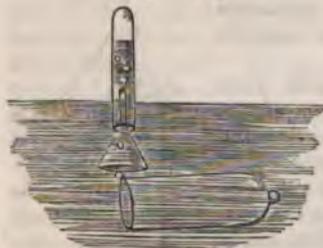
In selecting graduated apparatus, it is always advisable that they should be graduated to one standard. Thus, if the tubes and jars be graduated in cubic inches and their fractions, the measures should be divided into pints, ounces, &c.; or, if the tubes be graduated to the continental scales, the measures should be so likewise, since this saves much calculation.

The measurement of gases should be effected upon a very firm and level table or shelf, which, in a well-conducted laboratory, should be reserved exclusively for these operations.

If the bulk of a gas, contained in any ungraduated vessel, has to be measured, it is transferred, in the manner above described, into a graduated vessel, and the space which it occupies therein ascertained.

If the gas is contained in a jar or bottle, it is transferred into a graduated jar, which is then depressed in the well of the trough until the surface of the water or mercury surrounding the jar corresponds to that within it, great care being taken to hold the jar in an upright position, so that, if the latter be graduated

Fig. 42.



upon the opposite sides, the graduations indicated by the surface on each side correspond accurately. In reading off the graduations indicated, the eye of the operator should be brought as nearly as possible to a level with the surface of the liquid in the jar. If the gas is contained in tubes, the operation is pretty much the same.

In reading off the graduation indicated by the surface of liquid in a jar or tube, attention must be paid to the following circumstances.

When the liquid used moistens the side of the vessel (as water), the surface of the former will be elevated where it is in contact with the vessel; should mercury be used (which does not moisten the glass), there will be a depression of the surface round the sides; it is in both cases necessary, for correct measurement, that the eye be brought to a level with the general surface of the liquid.

In order to secure the position of the vessel, in which the gas is measured, being perfectly upright, it is well to suspend two plumb-lines (which may consist of any heavy body attached to a string) in the neighborhood of the trough—the one opposite to the position taken by the operator, the other to his right or left side—the vessel should be so placed that the sides are parallel to the plumb-lines.

In reading off any bulk of gas, when accuracy is required, it is necessary to note the state of the thermometer and barometer at the time, and the temperature of the air and water should agree within a degree or two at the time of operating. It is then necessary that the volume of gas observed should be submitted to certain corrections for temperature and pressure of air, in order that the results obtained at different periods may be compared. For the methods of effecting such corrections, the reader is referred to the method of taking the specific gravity of vapors (§ 8).

There is but little difficulty in measuring out larger quantities of a gas for any specific purpose. A graduated jar is filled with water, and the gas passed or transferred into it in the ordinary manner, until it contains nearly the required quantity. The remainder must then be added very gradually, by means of a lipped vessel or delivery-tube with a narrow opening, so that the amount of gas introduced at one time is but small. Observations must be made from time to time, whether a sufficient quantity has been introduced, by lowering the jar into the well of the trough, and reading off in the usual manner.

Great care is required in measuring out smaller quantities of gases into tubes when much accuracy is necessary; the gas must be delivered into them slowly and in much smaller quantities; but in other respects the operation is the same as above described.

§ 36. SOLUTIONS OF GASES in various liquids are of great use in the laboratory as reagents; it will therefore be well to say a few words upon the method of preparing them.

If the quantity of gas to be absorbed be considerable, it is advisable to divide the solvent into three or four portions, introducing each into a Woulfe's, or wide-mouthed bottle, and connecting these with each other and the generating apparatus, in the manner directed for the construction of a purifying apparatus (§ 28). If the gas be very soluble in the liquid employed, the bubbles, as they enter the first bottle, will be perfectly absorbed, or they will be reduced considerably in size as they leave the delivery-tube, and will gradually decrease as they pass upwards through the fluid. As soon as the liquid in the first bottle is nearly saturated, the bubbles will decrease but slightly in size as they pass upwards, and a portion of the gas will pass over into the second bottle, where it will in turn be perfectly absorbed, and thus the operation is continued until the bubbles, as they pass through the liquid in the last vessel, no longer decrease in size. It is advisable to attach a tube to the last bottle, by which any gas that

is not absorbed may be conducted into a glass vessel containing a quantity of the same solvent, or any other liquid that may absorb the gas more freely.

When the quantity of gas to be absorbed, or liquid to be saturated, is smaller, the latter should be contained in a tall narrow jar, and the delivery-tube be allowed to pass to within a quarter of an inch of the bottom; the bubbles of gas, in ascending, are thus brought into contact with a very large surface of liquid, and the absorption is consequently far more perfect than if effected in shallow vessels.

When gases are to be separated by the absorption of one or more, by means of various substances, the same apparatus as those above mentioned should be used. Very ingenious apparatus have been contrived for absorbing gases in accurate experiments; these are particularly useful when the quantity of gas absorbed is to be determined. Their forms are various, but they nearly all consist of several glass bulbs, connected in various positions by means of narrow tubes, and nearly filled with the absorbent. The gas, if not completely absorbed in passing into the first bulb, ascends, or is forced by the pressure of gas in the generator, through the narrow connecting tube into the second bulb, and so on, until it can no longer escape absorption. *Liebig's potassa-apparatus* (Fig. 43) is the most important and useful of these.

Fig. 43.



A very ingenious method is resorted to for the separation of mixtures of gases in eudiometrical experiments, by absorption. A small ball (about as large as a pea) of the substance having an affinity for the gas to be absorbed, is cast or moulded (with the aid of a little water or gum, if necessary), round the extremity of a piece of thin flexible iron wire of considerable length. This ball is then introduced under water or mercury into the gas to be operated upon, which is contained in a graduated glass tube, the wire being pushed upwards into the tube until the ball protrudes above the surface of the liquid. When absorption has ceased, a fresh ball may be introduced, and every trace of the gas to be absorbed thus removed from the mixture. A second and third gas may be then absorbed in a similar manner, by means of appropriate balls.

Sometimes gases are absorbed in tubes over mercury by the introduction of liquids. A pipette, the long end of which is bent upwards at about two inches from the opening, is used for injecting the liquid into the tube. When charged with the absorbent, the mouth of the pipette is closed with the finger, and the lower opening introduced as far as possible into the tube, under mercury; the liquid is then forced up into the tube by blowing cautiously into the pipette. Too much force must not be applied, or the liquid will be at once forced into the tube, together with a portion of air from the mouth. A small portion of the liquid should therefore be retained in the pipette.

Fig. 44.



§ 37. CONDENSATION OF GASES.—The effect of powerful pressure, assisted at times by a great reduction of temperature, has been most successfully applied by Faraday, to the condensation of many gases to the liquid and solid states. The method employed by him for liquefying gases is to generate them in a confined space in the following manner: A tube of strong, tough glass (green bottle-glass) is sealed at one end and bent in the centre at an angle of about 130 degrees. The materials for generating the gas are then introduced, so as to occupy a portion of the closed arm of the tube,¹ after which the other extremity is hermetically sealed.

¹ If the gas to be condensed is of such a nature as not to be evolved by the action of heat upon the material employed, but by the chemical action of different substances on

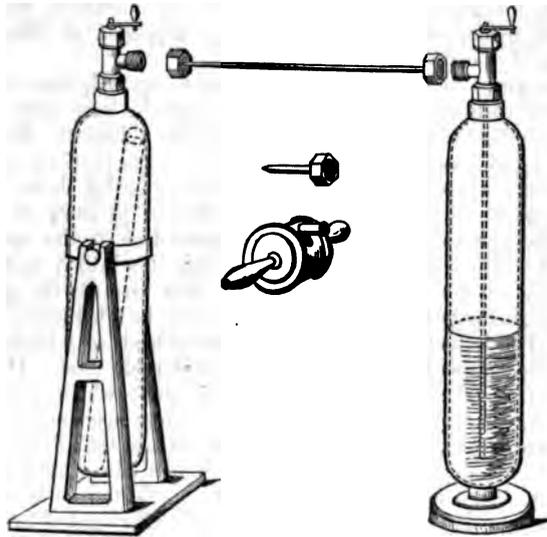
The gas is then generated, accumulating in the confined space; it gradually exerts a very great degree of pressure, whereby a portion becomes condensed to a liquid in the extremity of the tube opposite to that containing the materials. To facilitate the condensation of the gas, this extremity of the tube is surrounded with a frigorific mixture. The pressure at which the gas condenses is ascertained by a slender graduated tube or gauge, closed at one end, and containing, near the open extremity, a globule of mercury; this tube is introduced into the condensing tube, together with the materials from which the gas is generated. In proportion as the pressure exerted by the confined gas increases, the volume of air in the small tube decreases, the mercury being forced towards the closed end.

By this method alone, Faraday succeeded in liquefying the following gases: sulphurous acid, carbonic acid, hydrochloric acid, hydrosulphuric acid, chlorine, cyanogen, ammonia, and protoxide of nitrogen.

Subsequently, by employing very stout green bottle-glass tubes, curved so as to admit of their immersion in frigorific baths, and attached to powerful condensing syringes, Faraday obtained the following results: olefiant gas, the fluorides of boron and silicon, and phosphuretted hydrogen, were liquefied; hydrobromic and hydriodic acids were converted into crystalline solids, as were also, of the gases previously liquefied, hydrosulphuric and sulphurous acids. The following gases exhibited no indications of liquefaction when cooled down to -166° F. ($-74^{\circ}.4$ C.), and exposed to a pressure varying from 27 to 28.5 atmospheres: carbonic oxide, coal gas, binoxide of nitrogen, hydrogen, and oxygen.

Thilorier first succeeded in applying the principle of Faraday's gas condensing-tube, to the preparation of liquid carbonic acid upon a large scale. The appa-

Fig. 45.



atus contrived by him consists of two very stout cylindrical vessels of wrought iron or gun-metal, one of which acts as gas-generator, the other as receiver; the latter is fixed upon a flat foot, the former rests by trunnions upon an iron frame,

each other, the method of conducting the operation varies somewhat from the above brief description; we must refer for further particulars to large works on Physics, or to Faraday's published researches.

so that it may be tilted at pleasure. Both vessels are provided at the top with very accurate stopcocks or valves of a peculiar description, consisting of a tube with a lateral orifice, and containing a spherical plug of lead on a spindle, which is screwed down by means of a handle into a brass spherical cavity, having at the bottom an opening into the cylinder.

The generating cylinder is charged with $2\frac{1}{2}$ lbs. of powdered bicarbonate of soda and $6\frac{1}{2}$ lbs. of water at 100° F. ($37^{\circ}.7$ C.); these are well stirred together, and a long, narrow, copper tube is then introduced, containing 1 lb. 3 oz. of oil of vitriol; the top of this tube must be carefully rested against the side of the cylinder, so that none of the acid is spilled. The stopcock is then screwed on very firmly,¹ and the cylinder afterwards turned upon its trunnions so as completely to invert it; in this position it is retained a short time, and then turned over and over two or three times, by which means the acid becomes properly mixed with the other contents. The carbonic acid will of course be immediately generated, and collect in the upper part of the vessel with considerable elastic force. When the generator has been allowed to remain at rest for a short time, it is connected with the other cylinder or receiver, by means of a stout copper tube, which screws on to the lateral opening of the stopcocks. The receiver has a tube passing from the stopcock nearly to the bottom of the cylinder, and is kept surrounded by ice. When the connection is perfect, both stopcocks are opened, whereupon the carbonic acid passes over and liquefies in the cooled receiver. The cocks are then again closed, and the cylinders separated; any portions of confined gas in the generator are allowed to escape, the sulphate of soda is then emptied, and a fresh charge of carbonate, &c. introduced, as before. The operation is thus repeated five or six times, when the receiver will contain a considerable quantity of liquid carbonic acid. The greatest care is required in constructing and using this apparatus; under any circumstances, the operation is a dangerous one, several severe accidents having happened at different periods, by the bursting of the cylinders.

When the stopcock of the receiver is afterwards opened, some of the liquid carbonic acid will rush out, being forced up through the long tube by the pressure of the atmosphere of gaseous carbonic acid in the cylinder. Being a highly volatile liquid (§ 124), a portion instantly resumes its gaseous form upon escaping from the stopcock, whereby the remainder becomes cooled down to so low a temperature as to freeze, bearing a great resemblance to snow, as it falls from the mouth of the stopcock. If a nozzle be screwed on to the opening of the stopcock, and the liquid be allowed to escape from this into a metal box, provided with hollow wooden handles, the portion that assumes the gaseous state will escape through the latter, while the box will soon be filled with solid carbonic acid (§ 124). The latter, being a bad conductor of heat, may be handled without injury; it also retains its solid form for a considerable time. If mixed with a small quantity of ether, it yields a semi-fluid mass, which evaporates very rapidly, producing thereby the most intense cold; large masses of mercury may be frozen by these means, and it is this frigorific mixture that Faraday employed so successfully in his experiments with the gases just now alluded to. Several of those which he succeeded in condensing by the application of a comparatively moderate pressure, in his earlier experiments, were afterwards found by him to condense as readily by exposure to the frigorific action of the above mixture.

Another kind of apparatus, which is said to be perfectly safe, has been constructed by Natterer, for the liquefaction of carbonic acid. The gas is forced, by means of a forcing-pump, into a wrought-iron cylinder of considerable thickness, provided at the top with a valve like those of Thilorier's cylinders, and at

¹ Washers, or collars of lead, are used to insure the perfect tightness of the apparatus under the enormous pressure exercised.

the bottom with a spring-valve opening inwards. The gas is compressed into the cylinder by the forcing-pump, being admitted by this valve, through which none can again make its escape, since the spring only yields to external pressure. The cylinder is surrounded by another vessel, in which ice is placed.

DISTILLATION AND SUBLIMATION.

§ 38. These very important operations are comparatively simple in their nature, requiring almost the same apparatus. Their object is the separation of a body from extraneous substances by its conversion into vapor, its removal in that state, and its subsequent condensation. The operation is termed sublimation, if the resulting product is a solid, and distillation if it is a liquid.

The theory of the process of sublimation and distillation is simple enough, since it consists merely in raising the substance to be purified to a temperature at which it will pass over into the gaseous state, and conducting the resulting vapor into a receiver, the temperature of which is sufficiently low to cause it to return to the liquid or solid state. Nevertheless, the very different temperatures at which bodies vaporize, and at which they may be condensed, render it necessary that the apparatus employed should be modified to suit the various conditions, and that many precautions should be minutely attended to. We will first turn our attention to distillation, and consider the most important modifications of apparatus used in the laboratory for distillation at different temperatures.

DISTILLATION AT HIGH TEMPERATURES.

Some liquids require so high a temperature for their conversion into vapor, that their distillation must be effected over furnaces. Glass vessels cannot, consequently, be used for such operations, and recourse must be had to metallic vessels, or *stills*, as they are termed.

These consist, generally speaking, of a boiler to contain the liquid, to which is adapted a head, terminating in a beak, which fits into the condensing apparatus.

A cheap and very serviceable still of this description may be made of the common culinary digester, by removing the valve at the top of the lid and replacing it by a piece of iron pipe, bent like a siphon, at an angle of about 60°, the long arm being about sixteen inches, and the short arm six inches in length; the extremity of the latter is firmly screwed into the lid of the digester. When the boiler of the still has been charged with the liquid or solid to be distilled (the operation in the latter case is called *dry distillation*), the head is fitted on firmly. If the modified digester above described is used, it is well to fill the groove of the lid, into which the lower portion fits, with white-lead, which, as the former is hammered on, fills up all interstices, rendering the apparatus perfectly tight, even when under considerable pressure.

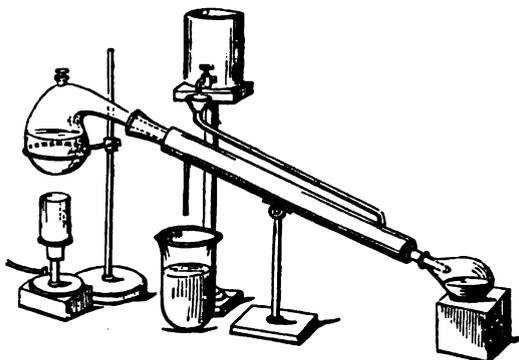
The next step is to fit the beak of the retort, or still, into the condensing apparatus or refrigerator. There are two forms of condensers in general use—the *worm*, and the *Liebig's condenser*.

THE WORM is generally used in larger operations, as it presents a much greater condensing surface than Liebig's tube. It consists of a spiral pipe, generally of metal (tin being in most cases preferable), inclosed in a tub, and surrounded with cold water; the lower extremity passing out at the side of the tub in the form of a spout. The upper extremity, which likewise protrudes through the side of the tub, is generally widened, and conical in form, so as to fit upon the beak of the retort. Should the latter be too large for introduction into the worm, it is necessary to fit upon it a conical tube of metal or glass, which is

termed an *adapter*, the thin extremity of which is sufficiently small to enter the condenser. It is advisable to lute all joints in an apparatus of this description with white-lead, as the temperature of the portion near the still-head is frequently so high as to char corks rapidly. In order to effect perfect condensation of the vapors evolved, it is necessary to allow a continual supply of cold water to replace that in the tub, as it becomes warm from the quantity of heat communicated to it by the condensed vapor. The best of many contrivances to effect this, is that of supplying a continuous stream of cold water at the bottom of the tub, and removing a corresponding quantity from the top. Great care must be taken that at least two-thirds of the condensing tube be kept perfectly cold during a distillation.

LIEBIG'S CONDENSER.—When the distillation to be performed is not on a very large scale, or the volatilized substance is condensed with comparative ease,

Fig. 46.



the Liebig's condenser may be used with advantage, as it is far more simple in construction, requires much less water to effect condensation than the worm, and is more easily cleaned than the latter. It consists of an inner tube (of glass or metal), surrounded by a metal tube of considerably larger dimensions; a stream of cold water is kept continually passing through the space between the two tubes, the points of ingress and egress of the water being similarly situated to those in the worm-tubs.

§ 39. **RECEIVERS.**—Various forms of vessels may be employed as receivers; the principal point to be attended to is, that the receiver be of sufficient capacity to collect the products of the distillation. Large wide-mouthed bottles or flasks may be employed as receivers; in the place of these, other forms of apparatus are frequently used, consisting of glass globes of various sizes, provided with one or more necks. If the globe is furnished with several openings, one of these should be wider than the others, and of a conical form. Such vessels are called *tubulated receivers*. The *quilled receiver* consists of a globe provided with a conical opening and a long tube, tapering off very much towards the end. This receiver may be fitted into a bottle by means of this tube or quill, which is made to pass nearly to the bottom, and allows the condensed products to flow from the globe into the bottle. Should globe-receivers or flasks be employed for collecting the products of a distillation, they should be very loosely fitted on to the delivery-end of the condenser by means of a large cork, to prevent their falling away from the former; they may also be placed upon rings of wood, or iron, covered with list, which are very useful for supporting flasks and retorts upon the table.

Distillations at high temperatures, or dry distillations, are frequently accompanied by the disengagement of gases, which it is sometimes necessary to collect. In such cases, the receiver must be fitted air-tight upon the mouth of the condenser, and provided with a tube properly bent, to serve either as a delivery-tube or connecting-tube, to which any purifying apparatus may be attached. It frequently happens that the cooling powers of the condenser employed are insufficient to effect the perfect condensation of the product, in consequence either of the great volatility of the latter, or of the rapidity with which the vapors are disengaged in the retort. In such cases, the lower end of the condenser should enter the receiver as far as possible, and the latter should be surrounded with cold water; for this purpose, it is placed in a basin of sufficient depth, filled with water; the upper surface, which cannot be immersed in the water, is covered with a piece of coarse blotting-paper or rag, upon which cold water is now and then poured.

Should a still lower temperature be required for perfect condensation, the receiver must be surrounded, in the basin, with a cooling mixture. If ice can be procured, it should be pounded up in a mortar, and then mixed with about half its bulk of salt. The receiver is then surrounded with this mixture, and the whole covered with a stout piece of flannel or cloth, to prevent the access of radiated heat, and render the cooling mixture effectual for as long a period as possible. If ice cannot be procured, other frigorific mixtures may be made by mixing together various salts in certain proportions, and adding water: *e. g.* 5 parts of nitrate of potassa, 5 parts of chloride of ammonium, and 16 parts of water.

DISTILLATION AT LOWER TEMPERATURES, BUT ABOVE 212°.

§ 40. When the temperature required for the volatilization of a substance is not very high, glass vessels are used for the generation of vapor; of these there are two kinds, retorts and flasks.

RETORTS.—For simple distillation, the form of the retort is not very important; it is desirable, however, that the neck should taper off gradually, and be tolerably long.

In selecting retorts, it should be observed that the inner concave portion of the bend be not sharp or in folds, and that the opposite convex surface be round. Great care must also be taken that the bulb or body of the retort is uniform, and moderately thin in substance, and as free from air-bubbles and spots as possible. A good retort should be thinnest at the bottom, and increase gradually, but slightly, in substance towards the neck.

Retorts are made both plain and tubulated. The former are more likely to stand any sudden change of temperature, on account of their greater uniformity; but the latter are far more convenient, as the operator has easy access to the interior. Tubulated retorts are generally fitted with glass stoppers, which, if they are ground in accurately, have great advantages over corks. The stopper should be slightly conical, and when moved in the aperture should feel perfectly firm and steady.

In charging a plain retort with a liquid or solid, a few precautions must be attended to. The neck of the retort must be perfectly clean and dry, so that no particles of a solid will adhere to it. The solid, in the state of lumps or powder, is introduced by means of a card, or of a funnel if necessary, so as to fall down one side of the neck, the latter being inclined at an angle of about 40°; the retort must not be held with the bottom of the bulb downwards, but inclined upwards, to prevent any lumps from falling suddenly upon it. A conical paper tube may also be used for the introduction of the substance. Liquids are introduced into plain retorts either through a funnel-tube, or piece of wide glass tube, sufficiently

long to reach the bulb of the retort and protrude two or three inches at the other extremity of the neck. During the introduction of liquids, the bottom of the retort should be inclined downwards.

Tubulated retorts are charged with greater ease through the upper aperture. Liquids are poured in through funnels sufficiently long to pass into the body of the retort below the neck; solids are either introduced through wide-necked funnels (their descent being aided by the introduction of a bit of wire in the neck, which is moved backwards and forwards), or if in the state of coarse powder or lumps, they are introduced by means of cards, which are either held to the opening by the hand and slightly agitated, or tied round the outside of the aperture, so as to form a very wide funnel. The neck of the retort should be inclined upwards, to prevent any of the descending solid from falling into and soiling it.

FLASKS.—The flasks used for distillation are the same as those recommended for the generation of gases (§ 23). When there is any great risk of the distillation terminating in the fracture of the vessel, as is frequently the case in dry distillations, Florence flasks are generally used on account of their cheapness.

These and other flasks, employed as retorts, are fitted by means of cork and luting with a wide tube, bent at a somewhat acute angle, the longer arm of which passes into the condenser. The short end of the tube, fitting into the flask, should not be above two inches in length.

If the vapor disengaged in the operation is very heavy, or easily condensable, great difficulty will be experienced in making it pass over the bend of the tube into the condenser. In such cases, the neck of the flask should be inclined considerably, and fitted with a tube as above, only bent at an obtuse angle; by this contrivance, the vapors pass over more easily.

In cases where the vapor condenses readily, before it passes the cork of the flask, and runs back into the latter, it is advisable that the bent tube should be sufficiently wide at the short end to admit of the neck of the flask being tightly fitted into it; the longer end should taper off gradually, like the neck of a retort; in fact, the neck of a broken retort, properly bent, answers very well for this purpose.

If the substance to be distilled be fluid or semi-fluid, or if it is likely to swell up from the disengagement of a gas, or ebullition, the retort or flask used should not be filled more than one-half; but if there be no such risk, the charge may be allowed to fill two-thirds of the body of the vessel.

For the condensation of volatile liquids, distilled from retorts or flasks, the Liebig's condenser is always employed, and the receiver surrounded with a cooling mixture, if necessary. If the product be easily condensable, a long, wide glass-tube may be substituted for the condenser, and, if necessary, wrapped round with strips of coarse blotting-paper, which are moistened from time to time with cold water.

In very small operations, such tubes may even be employed for rather volatile liquids, a little ether being substituted for the water with which the paper is moistened.

If the neck of a retort, or tube of a distilling-flask, is sufficiently small in dimensions in comparison to the wide opening of the condenser or adapter, it may be fitted into the latter by means of a perforated cork and luting. In many cases, however, the neck of a retort, if introduced far enough into the condenser, will fit the latter too closely to permit the interposition of luting or cork between the two.

A very tight joint may then be made, by wrapping a strip of bladder, which has been softened in warm water, three or four times round the spot where the retort-neck or tube and the extremity of the condenser touch; the apparatus should be steadied with the left hand, and the bladder, having been wrapped once round, pulled slightly with the other, to make it close tightly round the glass, and then

wrapped round again. Should the edges of the bladder not close upon the glass perfectly, they may be bound down to it by means of two very narrow slips of bladder, applied in the same manner, or may be tied with string. A joint of this description is very firm and tight when dry, as the bladder then contracts considerably. It is, indeed, always advisable, if possible, to make use of this description of joint in distillations, as in many operations, the cork, and even the lute, will be attacked by the vapors disengaged, and the tightness of the joint soon destroyed; the products of the distillation will also frequently become tinged, by dissolving minute portions of the cork. In the distillation of strong acids, it becomes necessary, however, to effect the junction with bladder coated internally with plaster of Paris.

In distillations of very small quantities, little retorts, blown before the lamp out of moderately wide glass tubes, are used; these may also be replaced by short, wide test-tubes, provided with a bent tube. Similar tubes may then also be conveniently used as receivers, since they may be surrounded to a considerable depth by a cooling mixture.

In some cases, where the distillate is to be permitted to return continually to the retort, as in digestions, or operations requiring some time for their completion, it is well to reverse the ordinary direction of the retort-neck and condenser, allowing these to point upwards, so that the condensed vapors may flow back again.

§ 41. *The proper application of heat in distillation* is the most important point upon which the safety and success of the operation entirely depends.

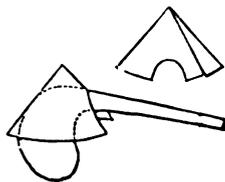
The retort or flask is placed upon a sand-bath, and the upper portion properly supported by the ring of a retort-stand, or some other support, in such a manner, however, that it will admit of being slightly moved about.

If a somewhat higher temperature is required than is procurable by sand-heat, the wire-gauze support may be substituted for the sand-bath. Before heat is applied, great care must be taken to ascertain that the outside of the vessel, and the sand employed, are perfectly dry, or great risk will be incurred of the flask or retort cracking as the temperature becomes somewhat high. Heat must be applied very gradually at first, and slowly increased until the liquid boils, or the distillation has fairly commenced, when the full heat requisite for the operation may be applied.

The flame of the lamp employed must never be allowed to reach any portion of the glass vessel beyond that which contains the substance to be distilled, lest it be cracked by coming in contact with the cooler liquid. Great care must be taken to keep the retort and the lamp out of the reach of any draught; a current of cool air, on approaching a hot retort, will very frequently cause its fracture, and, at any rate, the flame of the lamp, on being blown about by a draught, is very likely to touch the sides of the vessel, and cause fracture, as above stated; it is therefore advisable to protect the body of the retort and the lamp by means of a screen.

Much waste of heat, and sometimes also of material, arises from the partial condensation, in the upper part of the retort, of the vapors disengaged in the lower part, owing to the great difference of the temperature. When the temperature has been raised to the highest pitch, the liquid returning to the bottom of the retort will frequently undergo decomposition. This loss may be avoided, by covering the upper portion of the retort with a hood or cone of thick paper, cardboard, flannel, or better, of tin-plate—a contrivance which prevents radiation, and saves much heat. When a distillation is finished, the lamp is extinguished; but the retort is allowed to remain

Fig. 47.



upon the hot sand or gauze, so as to cool down very gradually; the bottom should not be exposed to the air until it is nearly cool. The retort may then be disconnected from the remaining apparatus, and water or other solvents introduced for the purpose of removing any residue.

Much difficulty is sometimes met with in the distillation of various liquids, such as dilute alcohol, alcoholic extracts, or solutions of salts and oils mixed with water; the contents of the retort not boiling at all for one moment, and, in the next, bursting into vapor suddenly, and sometimes with such force as to eject the contents of the retort, and even to break the latter. This may be, in most cases prevented, or considerably diminished, by the introduction into the retort of angular fragments of glass or metal, or coils of metallic wire (platinum, copper, or silver being preferable). If two liquids are to be distilled together, such as oils and water, which are not miscible, but separate into two layers, long coils of wire, or pieces of wood, extending through both liquids, should be introduced into the retort.

These promoters of regular vaporization must, however, never be introduced while the liquid is hot, as they would, in most cases, occasion such an instantaneous and powerful disengagement of vapor as to cause great loss of the substance, and danger to the apparatus and operator.¹

DISTILLATION AT TEMPERATURES BELOW 212°.

§ 42. The form of apparatus employed for distillations at low temperatures is precisely the same as that already described; the only difference is in the application of heat to the retort. Instead of placing the latter upon a sand-bath, or wire gauze, it is placed in a vessel of copper or tin-plate, which is then nearly filled with water, a proper allowance being made for the expansion of the latter when heated. This vessel (which is termed a *water-bath*) is selected, if possible, of such a depth as to admit of the whole body of the retort or flask being immersed in water; a small ring of straw, or a piece of rag folded three or four times, is placed at the bottom of the vessel, so as to interpose between it and the metal. The water in the bath is then gradually heated by means of a lamp to the temperature required for the distillation of the substance, and its original bulk in the vessel kept up by the addition of water, until the operation is completed.

This mode of distillation affords the most convenient and safest means of removing alcohol or ether from extracts.²

DETERMINATION OF BOILING POINTS.

§ 43. The boiling points of many liquids afford a most valuable means of testing their purity, and separating them from each other. The latter object is effected by simply collecting in separate receivers the products that are observed to pass over at different temperatures during an operation.

This is consequently an easy method of separating a liquid from small quantities of impurities, provided they differ sufficiently in their boiling points.³

¹ It may be proper to mention that the distillation of oil of vitriol, which is attended with great danger of succussion, is effected by means of a furnace constructed for the purpose, in such a manner that the heat is applied to the surface of the liquid, the bottom of the retort projecting below the grate. The introduction of small pieces of quartz into the retort has also been recommended, to prevent succussion in the rectification of oil of vitriol.

² If an uniform temperature, somewhat above 212° F. (100° C.), be required for a distillation, saline solutions, boiling at the requisite temperature, may be conveniently employed. Sometimes even an oil may be substituted.

³ This process is generally known as *fractional distillation*.

The temperature of ebullition of a liquid may be ascertained by observing the degree at which it constantly boils, and repeating the observation several times with the product, in the manner to be presently described. In order to determine this point, it is necessary to have a thermometer in the retort during the distillation.

The thermometers employed for this purpose have the scale marked upon the glass, instead of being provided with a wooden or metal scale; they are round, and the mercury-bulb, instead of being globular, is elongated, and as nearly as possible equal in diameter to the stem. A good cork, fitting accurately into the aperture of the tubulated retort to be employed, is perforated so as to fit tightly upon the stem of the thermometer. It is then cut through on one side with a very sharp knife, and adjusted upon the thermometer, which can now be done with ease and safety in such a manner that the bulb of the latter, when fixed in the retort, reaches to within a quarter of an inch of the bottom. The retort having been charged with the liquid to be distilled, which must not occupy more than two-thirds its capacity, a small coil of platinum-wire is introduced, and the thermometer is then fitted into the retort, the two edges of the cork being pressed firmly together, while it is gradually screwed as far as possible into the aperture, care being taken to have the side of the thermometer on which the scale is marked facing the operator. The degrees are more easily read off when a piece of white paper is held behind the stem.

In determining the boiling point of a liquid, or for separating one liquid from another by their boiling points, the following general directions will be found useful:—

Great care should be taken that the retort and condenser or adapter, employed in the operation, be perfectly clean and dry before they are connected. Several stoppered bottles, or other vessels, as receivers, perfectly dry and clean, should be got ready before the operation, each provided with a plain label, upon which any remark may be written.

The first portion of any liquid distilling over is likely to contain impurities; the thermometer will therefore be observed to rise gradually until these have passed over, together with some of the liquid. As soon as the thermometer has remained stationary for about half a minute, the first receiver is changed for a fresh one (the temperature being marked upon the former, between which the liquid it contains passed over); the distillation is then proceeded with until the temperature again rises; an increase of five degrees is allowed, the receiver is then replaced by a third, and properly labelled. Should the thermometer again become stationary, the receiver is once more changed, and the product collected within the range of five degrees, as before. Towards the end of the operation, the temperature generally rises rapidly, and the product is frequently colored, owing to the decomposition of some of the substance in the retort. Those products that have been collected at a definite temperature are generally rectified once or twice more in the same manner, the first and last portions being collected separately from that which again passes over while the thermometer remains stationary.

In each successive rectification, the range of temperature will be observed to decrease considerably. The receiver must always be marked with the temperatures between which the liquid they contained passed over, directly they are removed from the apparatus, in order to avoid errors.

The boiling points of liquids distilling below 212° are taken from the water-bath in the manner already described.

It is advisable, before submitting a liquid to an operation of this kind, to allow it to remain for some time in contact with some desiccating agent, and even to rectify it afterwards over a fresh portion of the latter, previously to its distillation with the thermometer.

When the quantity of liquid to be distilled with the thermometer is very small, a tube retort may be employed, into which a thermometer is fitted.

SUBLIMATION.

§ 44. The apparatus generally employed for sublimation are retorts or flasks fitted with wide bent-tubes, flat evaporating-dishes, and earthen or metal pans.

The more volatile substances may be sublimed from retorts or flasks leading into proper receivers. The process is conducted like that of distillation, with this exception, that any cooling arrangements that may be requisite are applied to the receiver, into which the retort-neck or tube of the flask is inserted to some distance. Should the substance condense in the neck or tube, a gentle heat should be applied to the latter, by moving a spirit-lamp to and fro along it, until the product volatilizes again.

Substances requiring a higher temperature may also be sublimed from Florence flasks, by placing the latter in a deep sand-bath, and imbedding them in sand, which may be gradually raised to a very high temperature over a fire.

Sublimation may be performed by placing the substance in a basin, and covering it with another, in which water is placed; as the substance passes over into vapor from the heat applied to the lower basin, it condenses upon the cool bottom of the upper one.

A very convenient way of purifying substances by sublimation is to place them in a pan or crucible, the mouth of which is afterwards tied over with moderately coarse filtering-paper perforated with a number of pin-holes. A cone or cylinder of stiff paper, closed at one end, is then tied, or fixed with paste, round the edge of the vessel, to which heat is then applied. The vapors are purified from any mechanical impurities as they pass through the filtering-paper, and condense upon the inner surface of the cone or cylinder, from whence they may be removed with ease after the operation is completed.

In separating volatile substances by sublimation from other matters, it is advisable to powder the substance finely, and to mix it with from one-third to one-half its bulk of sand, previously to its being heated. The same precautions should be taken in the application of heat as those recommended in distillations.

Fig. 48.



DISINTEGRATION.

§ 45. It is frequently necessary, or highly advantageous, to reduce solid matter to a minute state of division by mechanical means. Various processes are resorted to for this purpose; large masses are reduced to smaller lumps, and even to a coarse powder, by the hammer, particularly if they are very hard. For this purpose the mass may, in some cases, be held lightly in the left hand, and struck smartly with the hammer; or, if the substance be very hard, or in smaller masses, it may be split or crushed upon the anvil. It is advisable, at times, to wrap the mass in two or three folds of cloth or thick paper, in order the better to retain the fragments. The blows applied should be smart, and their force gradually increased. Tough metals and alloys, which cannot be broken by mere hammering upon an anvil in the cold, are cut with nippers or a knife, if sufficiently soft and thin, or heated to redness, and struck in that state until they crack, when they may be completely separated in the vice.

If the metal or alloy is not so hard, and is required in a somewhat fine state of division, it may be reduced to that state by means of a clean hard file.¹

Substances are most frequently reduced from large to smaller lumps, or to powders of various degrees of fineness, by means of the *mortar and pestle*. This instrument is made of various dimensions and materials; the most common of the latter are iron, Wedgwood, and Berlin ware. The iron mortars are used for the reduction of very hard substances; those of stoneware should admit of the pulverization of most substances of average hardness, and the preparation of solutions, acid or alkaline. The pestle should, if possible, be of one piece; or if the handle is of wood, care should be taken that it is well-seasoned, close-grained, and very tightly screwed and cemented into the bottom. The handle should be of a proper size to admit of its being firmly grasped by the hand; the diameter of the lower part may be about one-fourth of the upper diameter of the mortar; its curve should be somewhat greater than that of the mortar. Small pestles and mortars made of agate are employed for the pulverization of very hard substances or small portions of matter. Very hard substances may also be conveniently reduced to powder by means of a *crushing mortar*, which consists of a stout steel cylindrical chamber, into which fits a cylinder sufficiently small to pass with ease into the cavity. The substance being introduced into the mortar, the cylinder is placed upon it, and then forced down by repeated blows of a hammer; a powder may thus be obtained of any degree of fineness, without any risk of the material being dispersed.

In breaking a substance in a mortar it should be struck with sharp and rapid, but not too powerful blows by the pestle. If the substance is tough, considerable momentum should be given to the pestle; but if brittle, it should be held lightly in the hand, and allowed to fall with little more than its own force. To prevent any fragments from flying out of the mortar as they are separated, the latter should be kept covered during the operation with a flat piece of mill-board, having a hole in the centre through which the pestle can pass; or a cloth, with a hole in the centre, should be drawn over the mouth of the mortar, and held down on one side with the hand.

§ 46. The substance having been broken up into small fragments is next *pulverized*. Instead of allowing the pestle to fall, as it were, upon the substance, it is forced down upon it by being made to press it from the side of the mortar towards the centre. The stroke should be continued in one direction while the mortar is turned slowly with the left hand; in this manner the whole of the substance will gradually come under the pestle.

When the substance is reduced to a coarse powder, the comminution is completed by trituration.

The quantity of substance placed in the mortar at one time should not be too large, so that coarse particles may not become imbedded in the fine portion, and thus escape trituration. Thus, when a lump is to be reduced to fine powder, it should be first coarsely pulverized, and then a small portion of this powder operated upon at a time, in order to reduce it to a proper fineness. Substances may be transferred to or from a mortar, or loosened from its sides, by means of a *spatula*.

Bone spatulas (flat paper-knives) may be used if the substance is not likely to affect them. Bright steel spatulas are also convenient at times, on account of their greater flexibility; they must, however, always be cleaned after use, carefully, or they will soon become unfit for this purpose. Should the material operated upon attack bone or steel, a spatula of platinum or palladium must be

¹ The particles of steel detached from the file in this operation may in some cases be removed by a magnet.

employed. Pieces of card or thick paper may also be substituted for the spatula, if the powder is coarse, or if the material is soft and perfectly dry.

When it is desired to obtain a powder of great and uniform fineness, the process of *levigation* is resorted to. This consists in adding water to the substance in the mortar when it has been rubbed for some time, mixing the powder well up in it, and then allowing it to stand for a short time; the coarse particles will descend rapidly to the bottom, while the finer remain a longer time suspended in the water, which is then poured into a deep basin or jar, and the fine powder allowed to subside, the heavier portion being left behind in the mortar, together with a little water. This is again subjected to trituration for some time, and the above operation repeated; the disintegration of the coarse portion is proceeded with in this manner until nothing is left in the mortar. As soon as the water has become quite clear, it may be poured off, and the powder dried. It is sometimes necessary to submit the powder thus obtained to a second set of operations similar to the above, to obtain the requisite fineness.

Many metals which are required in small fragments may be reduced to the proper state of division by *granulation*. The metal is melted in a crucible, and when perfectly liquid, poured from a height of three or four feet into a pail, or other deep vessel, filled with water.

The crucible should be moved about while the metal is poured out, so that the granular fragments may be dispersed over the bottom of the vessel, as they would otherwise adhere, forming a coherent mass of granulation which is more or less difficult to separate.

Chemical means are frequently resorted to for the reduction of gold, silver, copper, platinum, and lead, to a fine state of division.

Gold may be obtained in a pulverulent state by boiling its tetrachloride with a solution of oxalic acid, or by mixing it with a solution of sulphate of iron; silver, by the introduction of a plate of copper into a solution of its nitrate, and brushing the metal off from the plate as it is deposited; lead, by the introduction of a plate of zinc into its slightly acid solution; platinum, by heating the ammonio-chloride of that metal to redness in a crucible;¹ copper, by the immersion of a piece of clean iron in its solution. All the metallic powders thus obtained, excepting platinum, require to be purified by repeated washings.

SOLUTION, INFUSION, DIGESTION, SATURATION, ETC.

§ 47. SOLUTION is of two kinds; it is either effected by liquids which exert no chemical influence upon the substances dissolved, or by such as alter, to a greater or less extent, their chemical condition. To the former class belong water, alcohol, ether, volatile and heavy oils, to the latter the principal acids.

The most important solvent is water; the others are only resorted to when its application is ineffectual, or its solvent powers insufficient.

Various means may be resorted to for *ascertaining the solubility of a body*; the most simple and effectual method in the case of solids, is to expose a small portion of the substance to the action of the solvent, with the aid of heat, to separate the liquid (two or three drops sufficing) by means of a filter, from any portion of the substance that is not acted upon, and to evaporate it slowly and at a low temperature in a small porcelain or platinum vessel, or on a platinum spatula or piece of flat foil; should any residuum be obtained, it is clear that the solvent has acted upon the substance, or some portion of it. *The solubility of a liquid* may be indicated by agitating a small portion of known bulk of the

¹ The finely-divided platinum thus obtained is termed spongy platinum.

latter together with the solvent, and observing whether, after the liquids have been properly mixed, any separation takes place, or whether the substance to be dissolved has decreased in bulk. *The solubility of a gas* may be ascertained by observing whether the bubbles passing through the solvent diminish in size, or whether, on agitating a portion of the gas in a closed vessel together with the solvent, absorption takes place. The solvent power of a liquid, at ordinary temperatures, is generally increased more or less by the application of heat.

Numerous kinds of vessels are employed for effecting solution. When the application of heat is not required, the substance may be dissolved in stout glass vessels of various forms, test-glasses or lipped glasses, and jars may be used; should the substance require the aid of much agitation to effect its solution, it may be shaken together with the solvent in a stoppered or corked bottle of such dimensions as not to be more than two-thirds filled by the liquid.

The apparatus employed in the solution of substances by the aid of heat, are dishes and capsules, beakers, flasks, and stirrers.

DISHES.—These are made of various materials; those of earthen and Wedgwood ware will answer for the solution of many substances not requiring the application of a very high temperature; great care must, however, be taken that they are compact in substance, so as not to absorb any solution that may be introduced into them. They should not become stained by solutions of sulphate of copper or of indigo. The best dishes are those made of Berlin or Meissen porcelain, since they are very compact, and thoroughly glazed. They should be lipped, and should be selected as thin as possible, varying from one-eighth to one-fourth of an inch, according to their size. When employed for effecting solution, these dishes should be chosen as deep as possible. The substance, and particularly the glazing, of porcelain and earthenware dishes, is attacked, and sometimes to a great extent, by the solutions of various chemical compounds; in such cases it is necessary to have recourse to dishes of silver, or even small dishes or capsules of platinum. These should be provided with a lip.

BEAKERS.—These glass vessels are exceedingly useful for effecting solutions, since they are generally very thin and uniform in substance, and made of well annealed glass.

They are also very tall in proportion to their diameter, which is likewise a great advantage. They may be had of various sizes, from two inches to ten or twelve inches in height, and of proportionate diameter. Great care must be taken that the bottoms be not thicker in substance than the sides, and that they are without the knot or *punty-mark* at the bottom. A flatter kind of beaker, provided with a lip, is also imported from Germany, and is very convenient for effecting solutions.

FLASKS.—The cheapest (and, in most cases, superior) flasks for dissolving substances, are the Florence oil-flasks; they have the advantage of being generally very thin at the bottom. When larger flasks are required, they should be of flint-glass; those of German manufacture are generally the best, on account of their uniformity of substance, and the goodness of the glass. It is more convenient to have flat-bottomed flasks for general purposes; the bottom should be uniform in thickness with the upper part of the flask, if not thinner; the necks should be rather wide, and provided with a projecting ring of glass, by which they may be securely held. If the flasks are round-bottomed, they may be conveniently supported on the table by the list-rings already referred to.

The **STIRRERS** employed are generally made of solid glass rod, from one-sixth to one-third of an inch in diameter, and four to ten inches in length. Their extremities should be carefully rounded off by fusion before the blowpipe. Some may be flattened, and others provided with a button of glass at the extremities.

§ 48. Solution may sometimes be effected in a mortar, by following the directions prescribed for levigation, and continuing the process until the whole of the

soluble substance has been removed from the mortar. Solution is always aided by previous mechanical division of the substance, particularly if only a portion of the body operated upon be soluble, the surface presented to the solvent being greatly increased thereby. Heat assists solution by increasing the power of the solvent, and also by establishing currents in the liquid, and thus continually exposing the substance to the action of fresh portions of the solvent. When the application of heat for effecting or promoting solution has to be continued for some time, it is advisable to make use of flasks which will retain more completely, and partially condense, the vapors evolved.¹

Some substances require continued boiling, or treatment at lower temperatures with the solvent, in order to effect their solution, or the separation of soluble from insoluble portions. In the latter case, the process is called *digestion*. Dishes and beakers are preferable when the substance requires agitation in the solvent by means of stirrers, or when portions have to be added or removed during the operation.

The vessel in which the solution is effected should be heated very gradually; it is always safer to protect it from the flame or fire by the sand-bath or sand-pot. When a temperature below 212° is required for solution or digestion, the vessel should be placed upon a water-bath.

All the precautions recommended in heating retorts in distillation should likewise be attended to in effecting solutions.

The addition of cold liquid to the hot contents of a basin should be effected very gradually (the latter having in all cases been previously removed from the source of heat), as, in descending rapidly, it would suddenly change the temperature of the bottom of the dish, and thus probably crack it.

A flask or dish is supported over the flame of a lamp by a tripod, or the ring of a retort-stand. Should the ring or tripod be too large, a triangle of strong iron wire may be placed across it, and the vessel firmly supported thereby. Should the contents of a flask be in danger of boiling over, the flask must be lifted away from the flame or sand-bath, the portion of it above the surface of the liquid being cooled down at the same time by blowing upon it; the vapor within will thus be, to a certain extent, condensed, and the ebullition diminished.

Small quantities of a substance may be dissolved in a test-tube. The latter should not be filled above two-thirds with liquid; it should then be held in an oblique direction in the upper part of the flame of a lamp; the fingers may be protected from the heat either by wrapping a thick piece of paper or cloth round the portion of the tube where it is held, and twisting the end together so as to form a handle, or by supporting it in the flame by means of a small metal clasp, with sliding ring and wooden handle, which is termed a *tube-holder*. In boiling liquids in test-tubes, the evolution of vapor is often very irregular and sudden, particularly when any dense solid is operated upon, the contents of the tube, or a portion of them, being frequently ejected in consequence; a slight and rapid agitation of the tube backwards and forwards in the flame will, to a great extent, prevent this.

When solvents boiling at low temperatures are employed, much economy of material is effected by partially closing the upper end of the tube with the fore-finger, the vapor being thereby prevented from escaping, and allowed to condense in the cooler portion of the tube. The tube should not, in such cases, be filled more than about one-third, and the flame of the lamp need only be applied at intervals, to keep up ebullition.

If the solution of a substance is accompanied by effervescence, it should be

¹ When somewhat volatile or precious solvents are employed, it is advisable to adapt a long wide tube to the mouth of the flask, in order that the condensed vapor may return to the latter.

effected in tall jars, or in flasks, in order to prevent the liquid from spirting over the sides of the vessel; the solvent should only be added gradually, that the action may not be too violent, and cause the liquid to froth up and overflow.

The very gradual addition of the proper amount of solvent, when considerable accuracy is necessary, may be effected by the washing-bottle, which will be described under the head of edulcoration.

Much difficulty is frequently experienced in pouring solutions from a flask, dish, or beaker, to another vessel, without spilling some portion. This may be

Fig. 49.



avoided by the following simple means: A glass rod, first wetted with the solution, is applied, in an almost vertical position, to the edge of the vessel containing the liquid, and its lower extremity allowed to dip into the vessel which is to receive the liquid; the full vessel is then gradually inclined, so as to allow the liquid to run down the rod in a steady stream; upon restoring the vessel to its original position, when the requisite quantity has been decanted, the drop of liquid that would otherwise run down the side of the vessel from the edge, is completely withdrawn by the rod.¹

Various terms are applied to the solution of organic substances, and their extraction from vegetable matters. *Infusion* is effected by pouring hot water upon the substance, and straining off the liquid; *decoction*, by digesting the substance for some time with the solvent, by the aid of heat; and maceration by pouring hot or cold water upon the substance, and allowing it to digest for some time. Soluble constituents may be conveniently removed from porous bodies by *lixivation*.

The substance is introduced, in the state of a coarse powder, into a large funnel, closed, at first, at the lower end of the neck, with a cork, and at the upper

¹ It is well, in addition, to grease slightly the border of the vessel containing the liquid.

end with a glass plate. Some large fragments of the substance to be dissolved, or a little plug of asbestos, or tow, are placed at the bottom of the funnel; these serve to retain the finer particles. The solvent is then poured upon the contents of the funnel, so as to cover the whole mass; the liquid, as it penetrates the particles, gradually takes up the soluble portions, and becoming dense, descends, making room for fresh portions of the solvent. After a time, the cork is withdrawn from the neck of the funnel, and the liquid collected as it drips through, being replaced in the funnel by the introduction of fresh quantities of the solvent, until the substance is exhausted. The use of the cork is in many cases unnecessary, when the soluble portion is easily extracted. This method is very convenient for the removal of vegetable principles from seeds and plants, and various forms of apparatus are in use for effecting extraction in this manner, under the name of *displacement-apparatus*, or *percolators*, the principal advantage of which over the simple funnel is that they prevent loss of the solvent by evaporation during the process.

§ 49. SATURATION.—A liquid is saturated with a solid or gas, when it has been charged with as much of either as it is capable of dissolving. The method of saturating liquids with gases has been described under the head of solution of gases (§ 36).

SATURATION OF A LIQUID WITH A SOLID.—A *hot saturated solution* is obtained by dissolving a moderate amount of the solid in the liquid, heated to the proper temperature, and then adding fresh quantities of the substance to the solution at intervals, until it refuses to dissolve any more, a quantity of the substance, consequently, remaining undissolved. Liquids generally dissolve a larger quantity of a solid, with the aid of heat, than they do at the ordinary temperature; the most expeditious way, therefore, of making a *solution saturated when cold*, is to prepare a hot saturated solution, to allow this to stand until perfectly cool, and to separate the portion of substance that has remained undissolved, or been deposited in the cooling of the liquid.

In order to ascertain whether a solution is saturated while hot, a drop of the liquid is transferred, by means of a glass rod, to a cold watch-glass, or piece of glass-plate; the deposition of crystals of a solid substance indicates the saturation of the solution.

This deposition may be promoted by stirring or agitation.

With some substances the application of heat is not admissible in the preparation of a saturated solution: in such cases the solvent is placed in contact with the powdered substance in the cold, in a stoppered bottle, or vessel in which it can be agitated. Should the whole of the substance first added dissolve after agitation, a fresh portion is placed in contact with the solution, and this is persevered in, either until there is no perceptible diminution in the bulk of the solid in the vessel, or, if accuracy is required, until the weight of a certain amount of the solid is not diminished by being left some time in contact with the clear solution.

FILTRATION, EDULCORATION, DECANTATION, AND SEPARATION OF LIQUIDS.

§ 50. The separation of solids from liquids is effected by *filtration* or *decantation*. The apparatus required for this purpose are funnels and funnel-stands, tall jars or beakers, stirring-rods, glass plates, and filtering-paper.

Filtrations on the large scale are performed in conical bags of flannel, or in pieces of linen cloth of moderate fineness, which are loosely strained over wooden frames, having been previously well soaked in water.

The form of glass and earthenware funnels should vary according to the ope-

ration to be performed with them. If it is wished to filter a liquid rapidly, the funnels should be ribbed; or, if plain funnels are used, the cone and neck should not join at a sharp angle. When the substance to be separated from a solution is in a state of very minute division, it is necessary that the cone and neck of the funnel should join at an angle of about 130° , and the former should taper gradually, and not bulge at the sides, so that the filter, when placed in it, may touch it at all points.

The funnel may be supported by the ring of a retort-stand, by tripod-stands, or by a wooden stand consisting of a flat board supported on four feet, about twelve inches high, and provided with round holes of various sizes. The lower extremities of the feet may be fixed into a piece of board corresponding to the top, to impart firmness to the stand.

Various kinds of *filtering-paper* are employed by chemists, according to the nature of the operation required. That most generally used, is the best white blotting-paper. When greater strength is required, a coarser, and much thicker kind of blotting-paper is used. All ordinary filtering-paper is, to some extent, contaminated with mineral substances, which do not, however, materially interfere in ordinary operations. At times, however, particularly in quantitative analysis, it is necessary to have the paper as nearly chemically pure as possible; the best paper of this description is imported from Sweden. The purity of filtering-paper is indicated by the quantity of ash which it leaves upon being thoroughly burnt. It is very convenient to keep the paper ready cut into circular pieces of various sizes. By folding these twice in opposite directions, the ordinary filter is obtained.

Rapid filtrations are effected by means of ribbed filters. If the filtering-paper employed is very porous, or the solid operated with heavy, or difficult to separate from the liquid, it is well to employ double filters.

PRECAUTIONS IN FILTERING.—The filter should in no case protrude beyond the funnel; its edge should be at least about a quarter of an inch below that of the latter.

Before throwing any substance upon a filter, the paper should be moistened with water (or any other solvent employed), by which means it is somewhat expanded, and the small pores existing in it thereby considerably contracted; if the substance is poured upon the filter without first attending to this precaution, a portion of the solid will frequently pass through the paper; and small particles are more liable to fill up the pores in the latter to such an extent as to cause the liquid to run through very slowly. The filter should never be quite filled with liquid, and the substance to be filtered should be poured on gradually and against the sides of the filter. Should the first portions of a liquid not pass through the filter quite bright, they must be returned thereto; and this must be repeated until the liquid is perfectly bright, when it is collected in a clean receiver. The spirting occasioned by the fall of the liquid as it drips from the funnel into the receiver, may be avoided by approaching the beak of the funnel to the side of the vessel, when the liquid will trickle down as it filters through. It is necessary, at times, to filter solutions rapidly while hot. In such cases, it is advisable to fit the funnel into a larger one, by introducing into the beak of the latter a perforated cork, adapted to hold the neck of the smaller funnel, and to fill up the space between the two with hot water. A metal case, with a hollow cylindrical arm projecting laterally, and closed at the bottom, is frequently substituted for the large funnel, and is very convenient, as heat may be applied to the arm, which is, of course, filled with water, and the latter kept at the boiling point while the filtration lasts.

§ 51. Many solids are purified from soluble substances, by washing them with water or other solvents, either by filtration or decantation. In the former case, the solution is allowed to drain off the substance as much as possible before

water is added; the filter is then filled up with pure water, hot or cold, according to circumstances; and fresh quantities are added, as the filter becomes empty, until the solid is sufficiently washed. It is advisable in washing a solid, to

Fig. 50.



bring the whole of the substance together into one mass, and not to allow it to remain as a coating upon the sides of the filter. This may be conveniently effected by forcing a jet of water against the sides until it is detached and carried down by the stream. The apparatus employed for obtaining this jet is the *syringe*, or *washing-bottle*. There are two or three forms of washing-bottles; the most convenient is constructed in the following manner: a narrow-mouthed bottle or flask is fitted with two tubes, the one bent in the form of a siphon, the long arm of which passes nearly to the bottom of the bottle, the extremity of the short arm being drawn out to a narrow point (so as to deliver a fine stream of water); the other tube is bent at an angle of about 100° , its two arms are nearly equal (the longest about three inches in length); the shorter arm is fitted into the cork, so as just to project inside the bottle. On filling the latter with a liquid, inserting the cork and tubes, and blowing into the bottle through the short tube, the liquid is forced up through the long one, and passes out at the short arm with considerable force, in a small stream. By inverting the bottle, the air will enter through the long tube, and the water pour out of the smaller one, the opening of which is not contracted; some force may be imparted to the current of water thus obtained by blowing into the bottle through the narrow opening of the long tube. By throwing a jet of water against the sides of the filter, and varying its direction by a movement of the hand in which the bottle is held, the portion of solid that adheres to them may be detached and washed down towards the point of the funnel.¹

Some substances adhere so obstinately to the sides of the filter as not to be easily removed by the washing-bottle; they should, in that case, be detached by means of a glass rod with a round extremity, great care being taken not to damage the filter. With some substances, it is also necessary to stir up the mass upon the filter with a glass rod, in order to disturb the fissures that form in it, which would otherwise allow the water poured upon the filter to pass through them, without penetrating the greater portion of the substance.

In filtering off or washing a substance, it is advisable to keep the funnel covered with a glass plate, which serves to exclude any impurities that might otherwise fall into the funnel, and also to prevent evaporation if the liquid filtered is volatile (particularly in hot filtrations). Large crystals, or considerable masses of substance, may be expeditiously and almost completely separated from a liquid, by throwing them upon a funnel, into the neck of which a small piece of tow, or asbestos, or glass rod is introduced, allowing the liquid to drain off.

§ 52. DECANTATION.—Some solids may be separated from fluids, or purified by a process termed *decantation*. This consists in allowing the solid to subside to the bottom of the vessel (tall jars being most convenient), and removing the clear supernatant liquid either by pouring it off slowly, or by decanting it with a *siphon* or pipette. Glass siphons are best adapted for this purpose; their size and bore should be suited to the quantity of material operated upon; but little need be said with regard to their use. The mouth of the short arm should not be allowed to approach the solid too closely, lest a portion of it should be

¹ The washing-bottle is also very useful for adding small quantities of water or other solvents to a solid, in effecting its solution, or for washing it down to the bottom of any vessel when it adheres to the sides.

sucked into the siphon by the force of the ascending current. For small operations, where the liquid is to be decanted to a great nicety, it is advisable somewhat to contract the orifices of the siphon, in order to reduce the size of the stream. The long arm should be held by one hand, near the extremity, in such a manner that the thumb may be directly opposite its mouth when it is necessary to stop the current. When the supernatant liquid has been decanted from a substance, the vessel containing the latter is filled up with water, the substance is thoroughly suspended in it by stirring the two well together with a glass rod, and it is then allowed to subside perfectly, and the water decanted when clear; this operation being repeated until the substance is perfectly washed.

Small quantities of liquid may be decanted from solids with greater safety by means of the *pipette*, which consists of a narrow glass tube, contracted at one extremity, and provided with a large bulb at about three inches from the other end, which is bent, above the bulb, at an angle of 120° . By immersing the constructed extremity in the liquid, and applying suction to the other end with the mouth, it may be made to ascend into the bulb; when the latter is filled, the tongue is pressed tightly against the opening of the bent end, the pipette is then removed from the vessel, and the liquid transferred to a receiver.

Care must be taken not to allow the liquid to flow back when once in the pipette, as this would occasion a disturbance of the particles of solid, and thus prevent for a time the removal of the liquid.

This tube is also of great use for the *separation of two immiscible liquids*. The operation is similar to that just described, the pipette being introduced into the upper or lower liquid, so that its extremity reaches nearly to the bottom of the layer. It is well, in separating liquids in this manner, to introduce them first into long narrow glass jars or tubes, so as to contract the area of the column of liquid by increasing its height, and thus rendering the separation of the liquids by the pipette far easier and more effectual. This operation may also be effected in various other ways. Oils may be separated from water, in which they are insoluble, by throwing them upon a wet filter. The water will pass through, and the oil may then be removed by piercing a hole in the bottom of the filter. Glass funnels, of which the stem is furnished with a tightly-fitting stopcock (*separating funnels*), are also very useful for separating liquids. The stopcock being closed, the liquids are poured into the funnel, and allowed to separate perfectly. By then opening the cock, the lower liquid may be removed from the upper, care being taken to allow it to run through very slowly as it decreases in quantity, and to close the cock directly the upper liquid approaches it. These funnels are frequently made in the form of globes, provided with an opening at the top; the loss of liquids by evaporation is much decreased by their use. The siphon may also be used for the separation of liquids.

Fig. 51.



Fig. 52.



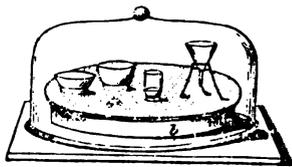
EVAPORATION.

§ 53. The apparatus necessary for evaporations are the same as those required for solution, with the addition of watch-glasses and small slips of glass. The dishes employed should, however, if possible, be more shallow than those used for making solutions.

Evaporation takes place at almost any temperature. When a liquid is allowed to evaporate slowly at the common temperature, it is said to undergo *spontaneous evaporation*. This species of evaporation is had recourse to principally in effecting crystallization, and in the desiccation of some substances to be presently mentioned. The vessel containing the liquid is covered with filtering-paper, to exclude any extraneous impurities, and then placed in a dry situation, where there is a continual access of air to remove the vapor as it gradually forms.

Spontaneous evaporation may be very much assisted by the use of desiccators.

Fig. 53.



The method most generally adopted is to place the vessel containing the liquid under a bell-jar, together with another containing sulphuric acid, which has a great affinity for water; or better still, to place these two vessels together under the receiver of an air-pump.

As the air is exhausted, the water passes readily into vapor, which is directly absorbed by the sulphuric acid, thus giving place to a fresh quantity of vapor, which is in turn absorbed.

The vessel containing the sulphuric acid should present a much larger surface than that containing the liquid to be evaporated, and they should be so placed that the latter is supported by the former. Other substances having a great affinity for water, may be substituted for sulphuric acid, such as chloride of calcium, fused potassa, or quicklime.

When the evaporation is effected by the aid of heat, it is applied in the manner directed for the solution or distillation of substances. When the evaporation is to be conducted at a constant temperature, recourse is had to the open water-bath already described, or to a similar bath filled with oil, if a temperature above 212° is required, a thermometer being retained in the bath to indicate the temperature during the operation.

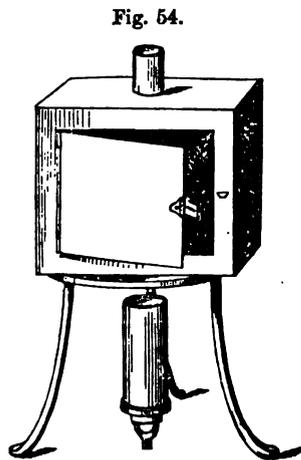
Evaporation effected below ebullition should be conducted in dishes (which should be kept covered by a piece of filtering-paper of proper size, through which a glass rod has been passed to act as a support): any crusts which may form upon the surface of the liquid should be disturbed from time to time, to prevent their retarding vaporization.

Evaporations at the boiling temperature are most safely conducted in flasks, as the liquid is thus prevented from spirting over the sides of the vessel: evaporation, when thus conducted, proceeds naturally much more slowly, as the vapor generated cannot escape so readily, and is also continually condensed to some extent. The same precautions must be attended to in the application of heat in evaporations as in distillation and solution.

In evaporating a solution to dryness, the residual mass should be diligently stirred, while the last portion of water is passing off; this considerably promotes evaporation, and lessens the risk of loss of substance from spirting. It is

generally advisable to expose the residue for a lengthened period to a comparatively low temperature, in order to expel the last traces of moisture.¹

§ 54. The expulsion of moisture from solid substances, is termed *desiccation*. This is effected at various temperatures, according to the nature of the substance. The greater portion of moisture may be removed mechanically from many substances, by pressing them, in a state of powder, between folds of blotting-paper. Some bodies require perfect desiccation at the ordinary temperature; these are exposed over a desiccating agent, *in vacuo*, until they no longer part with any moisture. Other substances are desiccated in the *water-oven*; a double metal box, between the sides of which water is contained, the temperature being maintained at 212° by means of a lamp placed underneath: the inner box is provided with apertures through which a current of air may circulate. For desiccation at higher temperatures we employ an *air-bath* (of which various forms exist), also provided with draught-holes and with a thermometer, so that the temperature may be properly regulated. Previously to desiccation, the substance is reduced to as minute a state of division as possible.



A crude test of its dryness after desiccation, is that of holding a cold clean glass plate over it while warm, and observing whether any film of moisture be deposited thereon. The most accurate test is, however, that of weighing the substance before desiccation, again ascertaining its weight after it has been exposed to the proper temperature for about an hour, and repeating the weighings at intervals of half an hour, until the last two agree with each other.

Some rather volatile substances may be desiccated by maintaining them at a moderate temperature, and at the same time passing a current of air over them. The substance is contained in a bulb-tube, one end of which is connected with a long chloride of calcium drying-tube (or with a wash-bottle containing oil of vitriol), the other with a tube leading into the top of a large closed vessel filled with water, and having one or two openings at the top for the reception of tubes (being kept closed when not in use), and a cock fitted into its side, near the bottom. Such a vessel is termed an *aspirator*. Upon turning the cock, the water will run out of the vessel and become replaced by air, which first passes through the chloride of calcium tube (where it is dried), thence over the heated substance into the aspirator, carrying with it any portions of moisture that may be given off by the substance operated upon. It is necessary to introduce a second drying-tube between the aspirator and tube containing the substance, lest the suspension of the operation should allow moist air to pass back into the tube.

When a substance has been perfectly dried, it should be at once transferred to a well-closed bottle or tube, in which it is preserved until required; unless this precaution is taken, the substance will absorb moisture to a greater or less extent in almost every case; some bodies absorb moisture rapidly at common temperatures, *i. e.* are *deliquescent*; these should be transferred as rapidly as possible

¹ It is often found convenient, in evaporating to dryness, to place the evaporating dish upon an empty tin pot, heated over a flame, the application of heat being thus rendered more uniform and gradual. Should the residue adhere firmly to the basin in which it has been evaporated, it is most easily removed by means of a spatula.

while warm.¹ Crystals and precipitates may be conveniently and expeditiously dried by spreading them upon two or three folds of blotting-paper, and then placing the latter upon a porous tile, which is replaced by a fresh one as it becomes saturated with moisture. In many cases these tiles may be first gently heated; they then effect the desiccation of the substance by promoting vaporization.

CRYSTALLIZATION.

§ 55. The property possessed by many substances of assuming definite and peculiar crystalline forms, frequently serves as a characteristic by which they may be recognized and distinguished from one another.

Crystallization also affords an easy and effectual method of purifying chemical compounds; it is generally effected by means of solution, fusion, or vaporization.

CRYSTALLIZATION BY SOLUTION.—A substance is crystallized from its solvent in one of two ways; by cooling the hot saturated solution, or by spontaneous evaporation. The first method is always resorted to when it is wished to effect rapid crystallization, the size and forms of the resulting crystals being of less importance than the purification of the substance. Those bodies which are less soluble in hot than in cold solvents are crystallized by the second method, which is also employed for procuring good crystals by gradual deposition.

A hot saturated solution, prepared according to the prescribed method (§ 50), is filtered, if necessary, as rapidly as possible (a hot-water funnel being employed when required), and allowed to cool undisturbed and gradually. If the solution is very concentrated, or has been agitated, or cooled rapidly, the crystals deposited are small, confused, and irregular in their forms; if it is wished to obtain regular crystals from a hot solution, the latter should not be too strong, and the above precautions should be attended to, in addition to which it is advisable to cover the opening of the vessel in which the crystallization is effected, to prevent evaporation on the surface of the liquid, and the consequent formation of a crust of confused crystals.

When the crystallization is to be effected by spontaneous evaporation, a saturated solution of the substance is prepared at the common temperature, and placed in a moderately shallow evaporating basin, which must afterwards be carefully covered with blotting-paper, unless the solution can be preserved in some place where no dust or impurity can reach it. Crystallization by spontaneous evaporation may be much assisted by placing the solution under a bell-jar, together with some rapid absorbent of moisture; or by introducing it under the receiver of an air-pump, together with a desiccating agent, and exhausting in the manner described under evaporation.

If crystallization is resorted to for the purification of a substance, the crystals obtained are separated from the solution (or *mother-liquor*) when perfectly cool, by gently decanting as much as possible from the crystals, and then throwing them upon a strainer or filter, and allowing the mother-liquor to drain off. A small quantity of the solvent employed is then poured upon them, and allowed to drain off, so as to remove the mother-liquor still retained by them. If, on applying the proper tests to a small portion of the substance, it is now found sufficiently pure, it may be at once dried for use. Should it require further purification, the crystals may be freed still more perfectly from the mother-liquor by pressing them between folds of blotting-paper, and then *recrystallizing*. This operation may be repeated until the resulting crystals are sufficiently pure.

¹ There are some substances which lose more or less of their water of crystallization at ordinary temperatures, *i. e.* are efflorescent; it is, however, always necessary, when they are required anhydrous, to submit them to desiccation by one of the above methods.

Substances may be crystallized from weak solutions (or mother-liquors) either by spontaneous evaporation, or by concentrating the solution with the aid of heat, until a small quantity placed upon a cold surface (a glass plate or watch-glass) deposits crystals upon cooling: it may then be set aside for crystallization.

The method generally resorted to for obtaining perfect and large crystals of the substance, is that of growing or feeding a crystal, as it is termed. A small and perfect crystal is selected from a crop obtained by one of the above methods, and placed in a vessel of moderate depth, containing a concentrated solution of the same substance, in the cold. The vessel is then covered with filtering-paper and set aside, where it is not likely to be disturbed. After the lapse of about twelve hours, the crystal is gently turned in the solution so as to rest upon another surface; and this operation is repeated regularly twice a day until the crystal has attained the desired size. As the solution becomes weaker it must be poured off, and replaced by a fresh quantity of the original strength. Great care must be taken that the solution be not too concentrated, since it most probably will then deposit fresh crystals, and very frequently upon the surfaces of the crystal to be fed; from which it is generally found difficult to detach them without injuring the surfaces of the large crystal.

MEANS OF PROMOTING CRYSTALLIZATION.—Two or three methods may be resorted to for promoting crystallization when it does not take place readily. The solution may be placed in a stoppered or corked bottle, or in a vessel the mouth of which may be closed by the thumb or the palm of the hand, and briskly agitated for two or three minutes; or the solution may be well stirred, and the sides of the vessel rubbed, with a smooth glass rod. The crystals obtained in both cases will be small, and generally speaking irregular; many substances, however, which would not be deposited from their solutions until after the lapse of some considerable time, may be made to crystallize out immediately by the above methods. The latter are, therefore, particularly useful in analysis, when it is wished to test for substances of this nature expeditiously.

Solutions which have remained for a considerable period without depositing crystals, may frequently be made to crystallize by the introduction into the solution of some angular fragment (a small crystal of some substance, or a grain of sand).

§ 56. **CRYSTALLIZATION BY FUSION.**—Several substances may be crystallized very beautifully by fusion. This is particularly the case with several metals, especially bismuth, and also sulphur, spermaceti, and other substances fusing at a comparatively low temperature, and capable of assuming crystalline forms. To effect crystallization by this method, the substance is melted in a flat ladle, and then placed upon a warm sandbath, so that it may cool very gradually; or the body may be first melted in a crucible, and then poured into a warmed flat vessel, and allowed to cool. When a tolerably solid crust has been formed on the surface, two holes should be pierced, at opposite sides of the edge, by means of a hot rod of iron; the substance that has not yet solidified in the interior is then poured out as rapidly as possible. When the mass in the flat vessel is cool, it is removed (which involves the fracture of the vessel, unless it be of iron), and very carefully cut open.¹ The interior will be found crystallized. Fine masses of crystals can only be obtained by this method when large quantities of the substance are operated upon.

CRYSTALLIZATION BY VAPORIZATION.—The principal directions for obtaining crystals by vaporization have already been given under the head of sublima-

¹ With such substances as sulphur or spermaceti, this is readily effected by means of a hot knife. Sulphur must not be heated too strongly, as otherwise it will become thick, and adhere to the vessel.

tion (§ 44). We have but to add that the more gradual the application of heat, the finer are the crystals obtained.

IGNITION.

§ 57. By this term is understood the exposure of a solid substance to a high temperature, for the purpose of altering to a certain extent its chemical or physical constitution. Some substances, ordinarily acted upon by solvents, are rendered insoluble by ignition; others are reduced to bodies of a more simple nature, by the expulsion of certain substances which are either volatile, or are converted by auxiliary means into volatile substances at elevated temperatures.

Some substances require, in their ignition, to be distributed over a considerable surface, in order that they may be exposed, as far as possible, to the action of the air. Such operations are generally conducted over the flame of a gas-burner, or powerful spirit-lamp, in thin flat dishes or capsules of porcelain, platinum, or silver. The heat should at first be applied very gradually (the dish or capsule being supported by a triangle or sand-bath), and care should be taken that the substances treated in this manner be thoroughly dried, and in many cases finely powdered, previously to ignition, in order to avoid decrepitation as much as possible. When it is desired to expose the substance thoroughly to the action of the air during ignition, it should be stirred from time to time with a piece of stout platinum wire, a platinum or steel spatula, or a glass rod (provided the temperature be not too high). Substances which require ignition in contact with air, and are likely to decrepitate or suffer loss from portions being carried away by the vapors evolved during the operation, should be heated in closed shallow crucibles (generally of porcelain or platinum), the lid being opened very slightly, to admit of the egress of vapor. At the close of the ignition, the lid may be partly or entirely withdrawn, and the access of air to the crucible facilitated by slightly tilting the latter, and holding the blade of a spatula, or the lid of a crucible, edgewise across the opening. It is also well, towards the close of the operation, to raise the temperature considerably by means of the blowpipe. Substances that require ignition out of contact of air, are heated in deep covered crucibles (of graphite or clay, according to the temperature applied). These are generally heated in furnaces; some substances of a peculiar nature are ignited over lamps, or by the blowpipe, in closed platinum or silver crucibles.¹ Before placing a porcelain crucible in a fire, or exposing it to the full flame of a lamp, it should be first gradually heated to some extent, to avoid the risk of its fracture by the sudden change of temperature. It is always advisable to commence the ignition with a gentle fire, and gradually to increase the temperature. A flat piece of fire-brick or tile (or an inverted crucible), should be placed between the bars of the furnace and the bottom of the crucible; the latter is then surrounded with fuel, it being generally advisable not to place any above the cover. In removing a crucible from the fire, it should always be first placed on some warm spot (*e. g.* the top of the furnace), that it may undergo no very sudden change of temperature. Iron tongs, of various forms and sizes, are used for handling crucibles. It is always advisable slightly to incline the crucible in seizing and lifting it with the tongs, especially when its weight is considerable.

In qualitative analysis, small quantities of substance may be ignited upon a

¹ These may be exposed over a lamp to a very high temperature, by placing them in an iron or copper *jacket*, consisting of a cone open at both ends, provided with projecting slips to support the crucible, and a second similar cone, the wide opening of which fits into that of the jacket. A silver crucible should only be heated over a spirit-lamp.

platinum spatula or scrap of platinum foil; when it is necessary to examine the matters given off during ignition, small portions of the substance may be heated in hard glass tubes, of moderate bore and about four inches in length, open at both ends, or closed at one extremity. The substance is placed at one end, about one inch from the opening (if an open tube is used), and then heated in the flame of a spirit or gas lamp (the tube being held more or less obliquely, according as a rapid or slow current of air is required to pass through it).

FUSION.

§ 58. The property common to a great number of solid bodies, of passing over into the liquid state at more or less exalted temperatures (*i. e.* their fusibility), is applied by the chemist for effecting certain physical or chemical changes which cannot well be brought about at ordinary temperatures.

Many compounds which obstinately retain water of crystallization, or constitutional water, at any temperature below their freezing-point, may be rendered anhydrous by maintaining them in a state of fusion for some time. (It should, however, be first ascertained that such bodies undergo no further decomposition at their fusing temperature.) When substances are operated upon which first fuse in their water of crystallization (undergo an aqueous fusion), the application of heat must be persisted in until the substance has first returned to the solid, and then again to the liquid state. Some substances are rendered more dense and compact in structure by fusion, which is at times a matter of great importance.

The mechanical division of other substances (particularly metals), is indirectly effected by fusion (granulation, *see* § 46). Fusion is likewise very frequently resorted to for decomposing or altering, to a certain extent, the chemical constitution of substances.

Frequently, other agents besides heat are called into action to effect chemical changes by fusion. Such agents are substances having an affinity for some portion of the body operated upon, converting it into a volatile substance, or combining with it to form some fusible compound. These are generally employed either when it is wished to reduce a metallic oxide or its compound to the state of metal, or to decompose insoluble compounds in such a manner as to effect their subsequent solution. Some substances are employed to convert certain metallic oxides into oxides of a higher class. These reagents (in what is termed "the dry way") have received the name of *fluxes*. They may be divided into four classes, according to their peculiar action: *reducing, oxidizing, double-decomposing, and simple fluxes*.

The most important reducing fluxes are, carbonate of soda or potassa, used together with charcoal, and in some cases alone; cyanide of potassium, and *black flux*.

The last is prepared by introducing gradually, in small quantities, into a crucible heated to a very dull redness, a mixture of two parts of cream of tartar and one of nitre. The resulting flux consists of a very intimate mixture of carbonate of potassa and charcoal, the latter resulting from the carbonization of tartaric acid.

Charcoal alone, although not a flux, is a powerful reducing agent; some oxides, or their compounds, fused upon or together with charcoal, are reduced to lower oxides or entirely deprived of oxygen.

Black flux is particularly useful in bringing the charcoal it contains into intimate contact with the substance to be operated upon.

The most important double-decomposition fluxes are, a mixture of three parts of carbonate of soda with four of carbonate of potassa; and hydrate of baryta.

The nitrates of potassa and soda are the oxidizing-fluxes.

The simple fluxes act sometimes merely as purifiers or protectors, removing any mechanical impurity contained in the substance operated upon; or, by being placed upon its upper surface, preserving it from contamination by any foreign matter during the fusion.

They also dissolve, in a singular manner, a number of metallic oxides, yielding with them slags or glasses of various and beautiful colors. The principal of these simple fluxes are, baborate of soda, or borax, powdered flint or green bottle-glass, and ammonio-phosphate of soda, or microcosmic salt.¹

It is in most cases essential or advantageous that these fluxes be perfectly dry and finely powdered before use. The simple fluxes may, perhaps, be excepted from this rule.

Fluxes should all be preserved in well-closed bottles, in order to prevent their absorbing moisture, or becoming impure.

§ 59. CRUCIBLES.—Fusions are performed in crucibles of clay, iron, graphite, porcelain, silver, or platinum.

Those of hard sandy clay (for example, the *Hessian crucibles*) are most frequently employed. If properly made, they will stand a high red heat, and are sufficiently dense to retain any liquid mass for some time. The great disadvantage of their use is their liability to be attacked by the fluxes employed, the substance operated upon becoming thus contaminated with silica or alkalis; the dissolving action of the flux upon the crucible is sometimes so considerable as to destroy its power of retaining the substance.

Iron crucibles may be sometimes substituted with advantage; these, however, cannot be used in a great number of cases, since iron is also very easily acted upon by most fluxes. When the fusion has to be effected at a very high temperature, *graphite crucibles* are employed; these act at the same time as auxiliary reducing agents (in consequence of the carbon which they contain).

Crucibles lined with charcoal are sometimes used in effecting reductions. Fine charcoal-powder is mixed up with thin gum-water, sufficient only to moisten it, without causing it to adhere. The crucible is lined with a coating of about a quarter of an inch in thickness, and the central cavity afterwards made as smooth as possible, by means of the end of a pestle. The reduction and fusion of iron is effected in crucibles prepared in this manner.

Fusions, and especially reductions on the small scale, are effected in crucibles of *Berlin* or *Meissen porcelain*, over gas or spirit lamps, by the aid of the blow-pipe. *Platinum* crucibles are substituted for these when a high temperature is required for the decomposition of a substance by fusion, or when the glazing of the crucible is likely to be attacked by the flux. They must, however, on no account be employed when the reduction of a metal is likely to be effected by the fusion, as in such cases the crucible would be inevitably destroyed, or very much injured. Caustic alkalis, or phosphates, and silicates, fused in the presence of carbon, likewise attack platinum; they may, however, be safely fused in *silver* crucibles.²

PRECAUTIONS TO BE ATTENDED TO IN FUSIONS.—A fusion is an operation requiring great care and constant attention: there is, indeed, no other process in chemistry so liable to casualties. The following is an enumeration of the principal precautions that should always be strictly attended to.

The special directions given with regard to the proportions of flux and sub-

¹ Bisulphate of potassa is a powerfully *cleansing flux*, on account of the free acid it contains, and it is particularly useful for cleansing platinum vessels. It is also sometimes employed for dissolving minerals; *e. g.* chrome iron-ore.

² *Gold* crucibles, alloyed with about five per cent. of platinum, are said to be much more convenient than these latter, since they stand a far higher temperature.

stance to be employed, their state of division, &c., must be always implicitly followed.

The *charge of a crucible*, and its size, must be regulated according to the nature of the fusion. Thus, if the operation is accompanied by the disengagement of a gas, or the swelling up of the mass, a capacious crucible must be used, and not more than half filled with the mixture. Substances diminishing in bulk upon fusion, may of course be heated in smaller crucibles, or in larger quantities.

The crucible must, in almost every case, be kept covered, but in such a manner that the lid may be easily removed at any point of the process, as it is necessary in most operations to examine the contents of the crucible from time to time.

The *heating of a crucible* must be conducted very gradually at the commencement, and care should be taken to have the source of heat as much as possible under control, so that the temperature may be lowered at any time, if the crucible becomes too hot, or the contents evince symptoms of boiling over.

If the operation is conducted in a furnace, it is frequently necessary to withdraw the crucible rapidly from the fire, placing it upon the top of the furnace, until it has somewhat cooled down. The heat should always be raised considerably towards the close of the operation. In many cases, particularly when reductions have been effected by fusion, it is advisable to sacrifice the crucible rather than to disturb the mass after it has been removed from the fire. In that case, the crucible, when sufficiently cooled down, is laid upon an anvil or stone slab, and smart blows are then applied to it, by means of a hammer, at a distance of about half an inch from the bottom. The fracture of the crucible is generally effected by this means in such a manner that the bottom separates from the sides, and any button of metal that may have collected there is then readily removed from the slag. When it is wished to preserve the crucible (those of porcelain, clay, &c. being referred to), the fused mass must not be allowed to solidify in it, even though capable of being afterwards removed by a solvent. Many fused substances, in the act of solidifying, endanger the safety of the crucibles; it is necessary, therefore, when the fusion is completed, to seize the latter firmly with the tongs, and to pour out the fused mass upon a cold, clean, and *perfectly dry* stone or iron surface; the crucible may then be placed in some warm spot, to cool gradually. In pouring out the mass, it is advisable to move the crucible about, so as to alter the direction of the stream issuing from it, thus spreading the mass over a larger surface. It then cools down more rapidly, and may be afterwards operated upon more conveniently than if it were in a thick mass.

In fusing any substance with nitre, when the oxidizing action of the latter is so violent as to be accompanied by deflagration, as in the oxidation of any organic substance, the nitre should be first heated alone until perfectly fused, and the substance then gradually introduced by means of a spatula, in very small quantities at a time. It is advisable to hold the crucible cover in the one hand, by means of the tongs, while the substance is being introduced, and to replace it immediately after every addition, in order to avoid loss by spirting. By employing a mixture of nitre and chloride of sodium, the former is rendered far more manageable—its action being thus greatly moderated.

Cyanide of potassium must on no account be employed as a flux when the substance operated upon contains any nitrate or chlorate, since a violent explosion would invariably result. In addition to the above directions, those given with regard to ignition should also be applied to the operation of fusion.

SOURCES OF HEAT IN THE LABORATORY.

§ 60. We will now consider some of the most important means employed for heating in the laboratory; since, by a due attention to these, the operator may not only effect a considerable reduction in expense, but, which is of infinitely greater importance, may considerably economize his time, and may attain that neatness in his processes which is so desirable for the analytical chemist.

LAMPS.—The simplest of all our sources of heat, which has been employed almost from time immemorial, is the common *spirit-lamp*, with which all our readers must be familiar; we should recommend them to be made of glass, with brass mounting for the wick; the plate carrying the wick-tube should screw into a brass socket cemented on to the lamp; a glass cap for spirit-lamps is to be preferred to one of brass, on account of its cleanliness. In extinguishing the lamp, the flame should be blown out before the cap is replaced, or the air within the latter is often rarefied to such an extent that considerable exertion is required to move it. *Wood-naphtha*,¹ in Great Britain, is the cheapest fuel for spirit-lamps; its flame should emit very little light, and should not deposit carbon upon porcelain dishes.

The heat of a spirit-flame may be much increased by supplying air to the interior; this is effected in the spirit-lamps of Berzelius and Mitscherlich, where the burner is constructed on the Argand principle, and the naphtha, or alcohol, supplied from a reservoir connected with the burner by a long narrow tube; these lamps produce a very high degree of heat, but are rather difficult to trim, and somewhat liable to get out of order; where gas cannot be had, however, they will be found very useful substitutes.

The *roaring-lamp*, which is described in the article on glassblowing, cannot be used in operations which occupy a considerable length of time; since it becomes too hot, and consumes an enormous quantity of fuel; but for rapid fusions, this instrument is very useful.

Oil-lamps are not very often used in laboratories, where their grease is very objectionable; the use of an oil-flame in blowpipe operations will be noticed hereafter; lamps for this purpose are usually made with two wicks, a round one for a fine blowpipe flame, and a flat wick for a large

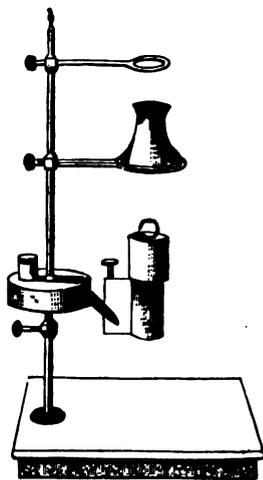
reducing flame; these should be very smoothly cut, and their snuff removed from time to time.

A good *Argand oil-lamp*, with a copper chimney, may conveniently replace gas in some operations on sand-baths, &c.

GAS, however, is far preferable to any other source of heat employed in the laboratory, and may be applied in a great many different ways; we shall give a brief description of two gas-burners which we have found most useful in practice. The most pre-eminent and important of these is the *gauze-burner*, which

¹ Also called pyroxylic spirit, or pyroigneous ether. In the United States, alcohol is used on account of economy.

Fig. 55.



consists of a cylindrical metal chimney (Fig. 56, *a*), about five inches high, and two inches in diameter, surmounted by a screw-ring, *b*, in which is fitted a piece of rather coarse iron-wire gauze; we have found that containing nine hundred meshes to the square inch very useful for this purpose. The burner which we are in the habit of using for such a chimney is a common Argand of $\frac{1}{4}$ inch diameter, carrying twelve holes, and provided with four arms to support the chimney; this Argand burner is screwed on to a plain jet, so that, if it be removed, a very good blowpipe flame is obtained; a heavy brass foot completes the stand, which is connected by means of a vulcanized tube with the gas-pipe, so that it may be moved to any part of the table. By removing the gauze ring, we may also obtain a very steady Argand flame.⁴

The gauze-burner acts upon exactly the same principle as the safety-lamp of Sir Humphry Davy, viz: that flame cannot be communicated through wire gauze of a certain fineness; within the chimney of the burner, the gas is mixed with an amount of air sufficient to burn the carbon and hydrogen simultaneously, so that no carbon is separated within the flame, and therefore no soot deposited; in fact, this burner not only equals the spirit-lamp in this respect, but also possesses the advantage of a much higher range of temperature.

The common ring gas-burner (Fig. 57, *a*, *b*), with sixteen holes, will also be found useful upon the working-table; that part of the latter which is in the immediate vicinity of the burner may be covered with a piece of sheet-iron, to protect it from the heat; an iron sand-bath of twelve inches in diameter may be very conveniently heated over such a burner; a ready support for sand-baths may be fashioned out of an inverted flower-pot, the bottom of which is removed, and square notches cut with a saw in the edges of the wide chimney thus formed.

§ 61. FURNACES.—It scarcely falls within our province to describe the various furnaces used by the chemist, but, when speaking of heating appliances, we cannot pass them entirely without notice.

A very good general furnace may be built of brick, the grate being arranged so as to insure a thorough draught, and so placed as to be easy of access to the operator; the furnace should be surmounted by a sand-bath of pretty large dimensions; either near to, or in connection with the furnace, there should be a combustion-table, covered with sheet-iron, upon which operations involving the use of redhot charcoal may be conducted; or this combustion-table may be constructed of brick, and a grate sunk in it supplied with air from beneath, and furnished with a movable conical chimney for increasing the draught; this grate serves to supply redhot charcoal. A drying-closet for filters, &c. may be conveniently placed, so that it shall be heated by the flue of the furnace.

⁴ A metallic ring, made to fit exactly over the wire-gauze, and with a hole of about an inch diameter in the centre, will be found useful to furnish a small flame for test-tubes, &c.

Fig. 56.

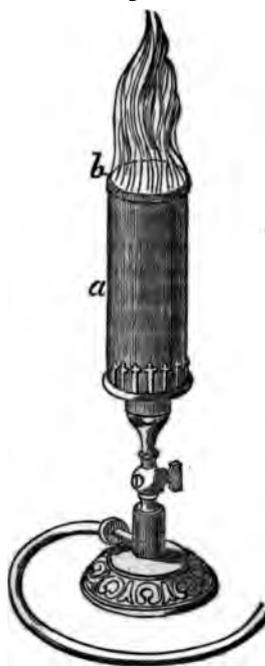


Fig. 57.



One of the best portable furnaces is that known as *Black's furnace*, which is made of sheet-iron, lined with fire-brick, with a wide iron pipe serving as a chimney, which may be conducted into the main chimney of the laboratory; this furnace is provided, in front, with two fire-doors, which give access to different parts of the fire; the ash-pit is closed by sliding-doors, which permit the regulation of the draught; there are also two holes, on the same level, at opposite sides of the furnace, to allow of the passage of tubes. A sand-bath is placed at the top of the furnace, and may be replaced by a deep sand-pot for operations with retorts, &c.; there should also be a lid with which the furnace may be closed for crucible operations.

In cases where small crucibles are to be raised to a very high uniform temperature, a piece of apparatus, termed a *muffle*, is employed; this is a nearly semi-cylindrical vessel of fire-clay, closed at one end, and furnished with long, narrow apertures at the sides, to allow of the radiation of heat into the interior, and of the passage of a current of air; this muffle is placed in the lower aperture of the Black's furnace before the fire is lighted, in order that it may be gradually heated to redness; the crucibles, &c. are placed on the bottom of the muffle.

An admirable furnace for operations where glass tubes are to be heated to redness, is the *combustion-furnace* (Fig. 58), employed in organic analysis; it is a

Fig. 58.



trough of sheet-iron, in length about two feet; in width, at the upper part, about five inches, at the lower, three, and in perpendicular depth, about three inches; the front of this furnace is closed with an iron plate, perforated with a hole of about three-fourths of an inch diameter for the passage of tubes, but the hinder end of the trough, *a b*, is left

open; the bottom is provided with slits, *D D*, made transversely at somewhat less than an inch apart, and between every other pair of slits, is placed a sheet-iron support for the tube. This furnace should also be furnished with several movable screens of sheet-iron (Fig. 59), serving to divide it into compartments, and with a cork-screen to hang on the front, in order to protect the corks from radiated heat.

Fig. 59.



When in use, the furnace must be supported over the combustion-table upon bricks, which, if needful, may be made to close partially the apertures at the bottom, in order to moderate the draught. The fuel employed is always *charcoal*, which should be of such quality as to burn without flame or much scintillation, and to remain redhot for some time after its removal from the fire; it should be used in rather large fragments, which maintain a brighter and more uniform fire than the small coals; the intensity of the heat may be increased, if necessary, by fanning with a piece of mill-board. The fire may be gradually enlarged to any extent by moving the iron screen farther from the front, which is very convenient in heating tubes successively throughout their whole length, as is requisite in organic analysis.

A portable *charcoal chauffer* will be found very useful for supplying redhot charcoal in such operations as that just described, as well as for affording a very uniform and manageable source of heat in various operations with flasks and retorts. It may even be used with advantage for heating porcelain crucibles, where a good gas-burner is not at hand.

A most convenient chauffer is a nearly cylindrical iron vessel, about seven inches in diameter at the top and six at the bottom, which is fitted with a grating; the sides are about five inches high, and are perforated with several holes of about $\frac{1}{4}$ inch in diameter, for admission of air; this chauffer should be supported on three legs, and provided with a conical chimney of sheet-iron, about eighteen

inches in height, which may be placed over it to increase the draught; if a few red-hot coals be laid at the bottom of the chauffer, then covered with charcoal, and the chimney placed on, a very brisk fire can be made in the course of a few minutes, especially if the draught be increased by the use of a pair of bellows. The small fire-clay chausfers now imported from the Continent will also be found very useful.

Little other furnace-fuel is used in the laboratory, besides coke and charcoal; the latter is only used in the combustion-trough and chauffer; *coke* being decidedly the best fuel for ordinary furnace-work. *Anthracite* is now much used for metallurgic operations.

THE USE OF THE BLOWPIPE.

§ 62. THE BLOWPIPE consists essentially of a tube of convenient size and shape, furnished with a small aperture or jet, through which a stream of air may be projected into the flame.

This instrument has taken a great many forms; the simplest of these is the common soldering-pipe (Fig. 60), used by braziers, which is a conical tube of brass or tin, of about one-third of an inch in diameter at the larger orifice, from which it tapers off to a jet of the required size; this tube is bent at a somewhat obtuse angle. Such a blowpipe, though not well fitted for analytical investigations, is often used in the laboratory for drawing glass, heating crucibles, &c., since its orifice is rather large, and it therefore furnishes a broad flame. The great defect of this tube consists in the want of a contrivance for preventing the projection of the condensed moisture from the mouth into the blow-pipe flame. This imperfection is remedied in *Black's blowpipe*, which is now generally used in analysis. It consists of a

conical tube of brass or japanned tin, the small orifice of which has a diameter of about one-sixth of an inch, and is fitted with a bone mouth-piece; the larger extremity is about half an inch in diameter, and is closed by a brass disk; at a distance of about half an inch from this end of the tube, another, but much smaller tube, about an inch and a quarter long, is introduced at right angles to the larger; this smaller tube is fitted with a perforated conical cap, called the jet, which may be removed to give place to a larger or smaller, as occasion may require. The jets are sometimes made of platinum, but more commonly of brass.¹ It will be seen that the portion of the blowpipe between the smaller tube and the closed extremity, forms a reservoir to contain the moisture which condenses in the tube, and thus prevents it from being projected into the flame. The smaller tube is sometimes terminated by a very fine aperture, so that no cap is required for the jet. A fine jet is necessary for analytical experiments, and a larger one for glassblowing, &c.

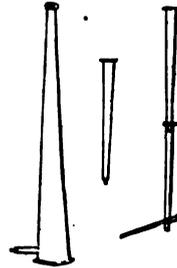
There are many other forms of the blowpipe, but the above is one of the least expensive, and is sufficient for all ordinary purposes.

¹ These jets are somewhat liable to be stopped; they may then be opened with a fine platinum wire, not with any sharp instrument, or the orifice will be too much enlarged.

Fig. 60.



Fig. 61.



Black's Blowpipe.

The *flame* which is best adapted to the use of the blowpipe in the laboratory is that of coal-gas, since it is perfectly free from dirt and grease, and admits of being regulated with great nicety. The gas should issue from a plain cylindrical orifice, of one-quarter to one-fifth of an inch in diameter; if the walls of the gas-jet be pretty thick, they afford a convenient rest for the blowpipe, for which a notch may be made in the margin of the orifice. When gas cannot be procured, a good oil-lamp, with a pretty thick, smoothly-cut wick, will answer the purpose; or a wax candle with a large wick may be substituted.

The principal *supports* used for the test-specimens in experiments with the blowpipe, are *charcoal*, *platinum wire* and *foil*, *iron spoons*, and *glass reduction-tubes*.

The *charcoal* selected for the purpose should be compact, free from cracks, and its fracture should be smooth and shining; it should not readily powder when struck, but tend rather to splinter; this charcoal must have been well carbonized, which will be indicated by its burning without flame or empyreumatic odor; it must not be "barky," or it will crepitate and scintillate in the blowpipe-flame, and when the latter is directed upon its surface, it should leave but little *white ash*; lastly, it should, of course, be perfectly dry. The good beech-charcoal in common use will generally be found to answer very well for blowpipe experiments; it should be split into pieces about three inches long and one inch in diameter, which are then ground flat and smooth on opposite sides by rubbing upon a rough stone.

The operator should be provided with a *small knife* to cut cavities in the charcoal, and with a *spatula* for lifting the fluxes, &c.; a small *pair of tweezers* for taking up metallic globules will also be found useful.

In some experiments, a *pestle and mortar of agate* are necessary; the internal diameter of the mortar should be about $1\frac{1}{2}$ inch, and its depth that of an ordinary watch-glass.

Two sizes of *platinum wire* should be found amongst the blowpipe apparatus; the thinner kind resembling a stout horsehair, the other having the thickness of the gut used for fishing-lines; these are cut into pieces of three and four inches in length.¹

Platinum foil must be so thick that a piece of it, two inches square, will not bend with its own weight; pieces of the above dimensions are suitable for most purposes.

Iron spoons are only used in rough experiments; they are generally rather thin in substance, round, shallow, about three-quarters of an inch in diameter, and provided with a long handle, which may be thrust into a cork to protect the hand.

Glass reduction-tubes are made of various forms, but are generally either simply closed at the end, or expanded into a bulb; the method of making these tubes will be described in the section on manipulation of glass; suffice it to say here, that they should be of hard German glass, in order better to resist the high temperature to which they are often exposed.

§ 63. *The chief reagents* employed in blowpipe experiments are the following:

Charcoal, which has been already mentioned as a support; it is sometimes required in powder, which should be strongly heated in a closed crucible, to expel volatile matters, previously to use. Charcoal is the chief agent employed for abstracting oxygen in operations with the blowpipe.

Carbonate of soda (NaO.CO_2) is often required in reduction-experiments, when its action appears to depend upon the momentary isolation of a portion of its sodium, which exercises a powerful reducing action on the substance operated

¹ These wires may be cleaned after use by boiling in conc. hydrochloric acid. They should be kept in distilled water.

upon. It acts also by extracting the acid from salts, and thus leaving the metallic oxide more exposed to the action of reducing agents, and sometimes serves to protect the surface of reduced metals, and to prevent their reoxidation.

Carbonate of soda employed as a blowpipe reagent, should, strictly speaking, be perfectly pure; but the common washing-soda of commerce, after one or two recrystallizations, is sufficiently so for ordinary purposes; the crystals should be thoroughly dried in a porcelain dish on a sand-bath, and afterwards rather coarsely powdered.

Black flux, which has been noticed when speaking of fusion, is also sometimes employed in blowpipe experiments.

Cyanide of potassium ($\text{KCy}=\text{KNC}_2$, prepared by Liebig's process) is very valuable as a reducing agent; most metallic oxides, when fused with cyanide of potassium, part with their oxygen to this salt, converting it into cyanate of potassa (KO.CyO); the great fusibility of the cyanide, however, prevents its application in many cases. This reagent should be used in the form of a coarse powder.

A rather strong solution of *nitrate of cobalt* (CoO.NO_2) is sometimes useful in experiments on charcoal.

Borax (*biborate of soda*, $\text{NaO.2BO}_3+10\text{Aq}$) is a most important blowpipe reagent. It should be finely powdered. The chief value of borax in blowpipe analysis depends upon its property of dissolving certain metallic oxides, forming glasses of peculiar colors. When heated in the blowpipe-flame, borax first swells up (intumescens), evolves steam, and then fuses to a perfectly colorless glass, which remains transparent on cooling.

Phosphorus-salt (*microcosmic salt*, $\text{NaO.NH}_3\text{O.HO.PO}_3+8\text{Aq}$) is sometimes used instead of borax for producing colored glasses. When heated, this salt loses its ammonia and water, and is converted into the metaphosphate of soda (NaO.PO_3), which fuses into a perfectly clear glass. Phosphorus-salt is used in small crystals.

Nitrate of potassa (*nitre*, KO.NO_2) is occasionally employed as an oxidizing agent; it should be kept in powder.

§ 64. It may be useful, in this place, to explain a few terms which are frequently used in describing the behavior of substances under the blowpipe.

INTUMESCENCE is the swelling up of the fused salt, in consequence of the rapid expulsion of its water of crystallization; borax affords a very good example of this (§ 63).

DECREPITATION has been already defined as the splitting up of the crystals of a salt, by the expansion of the mechanically-inclosed water.

DEFLAGRATION is the vivid combustion observed when powerful oxidizing agents are heated in contact with oxidizable substances (*e. g.* nitre upon charcoal), or when such agents are exposed to the inner blowpipe-flame.

DETONATION takes place when one or all of the substances acting upon each other are suddenly converted into the gaseous form, so as to give rise to a sharp noise.

INCANDESCENCE is the production of a bright light, when solid infusible substances are introduced into the hottest part of the blowpipe-flame.

§ 65. Before proceeding to describe the manipulations with the blowpipe, it will not be out of place to say a few words with regard to the *nature of the blowpipe-flame*.

In a coal-gas flame (which is quite similar to the flames of lamps and candles), the carbon and hydrogen which constitute the fuel, enter into combination with oxygen (forming respectively carbonic acid and water), but not simultaneously. The affinity of hydrogen being greater than that of carbon, for oxygen, under the present conditions, the former undergoes combustion first, leaving the carbon free in the midst of the flame, by the heat of which it is raised to so high a

temperature, that it emits a white light; this carbon afterwards undergoes combustion on coming in contact with the external air.

In a common flame, we may perceive three cones, the innermost of which (Fig. 62 A) is a hollow space, filled with combustible gas, whilst the second or luminous cone, B, is that in which the hydrogen undergoes combustion and the carbon is raised to a white heat, to be subsequently burnt in the cone, C, which emits very little light.

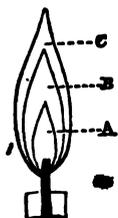
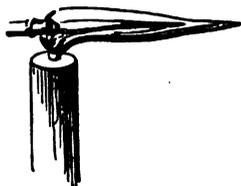


Fig. 62.

In examining the action of the blowpipe upon such a flame, it must be observed that the air projected into the latter does not proceed from the lungs, but is simply conveyed through the passages of the nose into the mouth, and thence ejected by a muscular effort of the cheeks, so that a stream of nearly pure atmospheric air (oxygen and nitrogen) is forced into the flame, to which enough oxygen is thus supplied to enable the carbon and hydrogen to burn simultaneously, in consequence of which no carbon separates, and the flame emits no white light.

The blowpipe-flame (Fig. 63), like that of the ordinary candle or gas-jet, consists of three parts; the inner hollow cone, where the cold air first passes into the flame; the inner cone of partial combustion; and the outermost cone, where the combustion is completed. In that part of the inner blue cone which is nearest to the blowpipe-jet, there must be an excess of oxygen, and in this place the combustion is perfect; beyond this, there is a point where neither the oxygen nor the combustible gas is in excess, and this is consequently the hottest part of the blowpipe-flame; this point is found near the extremity of the blue flame; a

Fig. 63.



little within the point of the blue flame (unless a very considerable amount of air be forced into it from a large blowpipe-jet), there will be an excess of combustible gas (carbon and hydrogen), which, at the high temperature to which it is here raised, is capable of abstracting oxygen from most metallic oxides, thus reducing them either to metals or to a lower state of oxidation. This part of the flame is termed the *reducing* or *deoxidizing flame*.

When the heated gas has passed the point of the blue flame, it is oxidized at the expense of the surrounding air, and gives rise to the very slightly luminous cone of complete combustion. Around this cone, then, there is an excess of oxygen, and if any substance be introduced into it which has any considerable affinity for this element, it will be at once oxidized; hence this outer cone has been named the *oxidizing flame*. The capabilities of the different blowpipe-flames may be readily tested by introducing a little oxide of lead, in a small iron spoon, into the inner flame, which will at once reduce it to the metallic state, and the metal thus obtained may be reoxidized by transferring it to the outer flame.

In order to obtain a well-defined blowpipe-flame with the gas-jet above described, the aperture of the blowpipe-jet should be placed just within the flame, immediately above the edge of the aperture from which the gas issues; if a reducing flame is required, a blowpipe with a small jet should be used, a larger orifice being better suited for oxidation. A broad scattered flame, which is very useful for heating crucibles, drawing glass, &c., is obtained when the blowpipe-jet is withdrawn to the distance of $\frac{1}{10}$ or $\frac{1}{4}$ inch from the margin of the gas-flame. A good blowpipe-flame should be free from white-light, and the two cones should be very well defined. The stream of air must not be intermitted, the operator acquiring, by continued practice, the habit of breathing through the nose without relaxing the muscles of the mouth and cheeks.

In examining the action of the blowpipe-flame upon test-specimens placed on charcoal supports, it is generally desirable to ascertain if any substance is *reduced* to the metallic state, and whether the surrounding portion of charcoal is covered with an *incrustation* of oxide resulting from the reoxidation of the metallic vapor in passing through the outer flame. To determine these points, a piece of charcoal having been selected and prepared according to the directions given above, a small shallow cavity (of about $\frac{1}{4}$ inch in diameter) is scooped with a penknife at one end of the smooth surface, within about half an inch of the edge, and in this the test-specimen is placed, and covered with the reagent to be employed; the charcoal is now held in the blowpipe-flame in such a manner that the reducing (inner) flame may be directed into the cavity, and the oxidizing (outer) flame allowed to flow over the surface of the charcoal, upon which it should extend itself in the form of a cone, within the limits of which we afterwards look for the incrustation; the stream of air must not be violent at first, or the substance will be blown away,¹ but should be increased as the operation proceeds. The specimen to be examined should be first powdered.

In some cases, especially in the analysis of minerals, it is necessary to *roast* the specimen, by exposing it for some time to the outer flame, to oxidize and remove sulphur, &c., before attempting to reduce it; this should always be attended to in the case of metallic sulphides, the carbonate of soda, or other reagent, not being added till the roasting is completed, which will be the case when the odor of sulphurous acid is no longer perceptible; the test-specimen should be turned about once or twice during the operation, to expose fresh surfaces to the oxidizing action.

The reduced metal is generally seen either in one pretty large globule or in a multitude of smaller particles, which may generally be induced to unite by judiciously directing the blowpipe-flame upon them; cyanide of potassium is very useful in favoring the union of such globules, since it becomes very liquid at a comparatively low temperature; the globules are best seen when the mass is red-hot. A globule having been obtained, it may be desirable to ascertain whether it is malleable or brittle; for this purpose, it is allowed to cool perfectly, and carefully removed with a pair of tweezers; having been placed upon the bottom of a strong inverted mortar, it is now struck sharply with the pestle, when, if brittle, it of course falls to powder (as in the case of antimony), if semi-malleable, it flattens out, at the same time breaking into several pieces (as with bismuth), and, if fully malleable, flattens out without breaking (like lead).

In some cases, and particularly where large quantities of earthy matters are present, small portions of reduced metal are disseminated throughout the mass after exposure to the inner blowpipe-flame, but will not join into globules; to detect these, the test-specimen, together with the surrounding portions of charcoal, may be scraped into an agate mortar, and reduced to a very fine powder; if this is submitted to repeated levigation, all the metallic particles will be left behind.

When looking for an incrustation upon the surface of the charcoal, it must be remembered that the latter is generally covered with a thin film of bluish-white ash after having been exposed to the oxidizing flame.

§ 66. A few metallic oxides are recognized by the color of their compounds with oxide of cobalt; in order to subject them to this test, the specimen is very strongly heated, on charcoal, in the hottest part of the blowpipe flame; it is then removed from the flame, moistened with a drop or two of the solution of nitrate of cobalt, and again very strongly heated; the color of the resulting compound should be observed when it has cooled, and by daylight.

The formation of *colored glasses* by dissolving certain metallic oxides in fused borax or phosphorus-salt, is often had recourse to as a means of recognizing

¹ This may be prevented by slightly moistening the substance.

them, and as such glasses usually present different appearances in both flames, every inference obtained in this way is supported by two indications. The colorless glass to be employed must first be prepared, and the oxide added to this by degrees, till a distinct color is produced; a piece of the thicker variety of platinum wire above mentioned is selected, and its extremity (previously well washed) bent round in the form of a loop, which should be somewhat smaller than the section of the reducing flame; this loop is now heated to redness in the flame, and plunged into the flux to be employed (borax or phosphorus-salt), when a sufficient quantity will adhere to it to form a small bead in the loop when fused in the blowpipe flame: in fusing the bead, the wire must be dexterously turned with the hand, to prevent the fused flux from dropping off, and the fusion is discontinued when the effervescence and boiling have ceased. The bead thus obtained, which must be perfectly transparent and colorless, and not larger than the section of the reducing flame, is now again heated to redness, and a very small particle of the substance to be examined made to adhere to it; the glass is fused in the outer flame (near the point) for some time, the bead allowed to cool, in order that its color may be observed, a fresh quantity of the substance added as before, and this operation repeated (always fusing in the outer flame) until either a distinct color is obtained, or a considerable amount of the substance has been added without affecting the color of the glass. The color (by transmitted daylight) of the hot and cold bead, should be carefully observed, and the latter then exposed to the reducing flame for some seconds, the color of the glass being afterwards again noted. It is obvious that the smaller the bead, consistently with distinct perception, the better; and that very little of the coloring matter should be added at once, since some metallic oxides impart such intense colors as, when in considerable quantity, to cause the bead to appear black.

Under metallic oxides are known by their imparting particular tints to the outer blowpipe flame, in consequence of the reduction and volatilization of the metal in the inner flame, and its subsequent burning with the color in question on arriving in the oxidizing cone. In order to test substances in this manner, a very small loop is made at the extremity of the thinner platinum wire, and well washed with distilled water: it is now introduced into the inner flame, and if it impart any tint to the outer flame, it is removed, after a few seconds, and again washed: this process must be repeated until the wire ceases to tinge the flame;¹ the loop is now unwashed with pure water, and a little of the powder under examination is added upon it and introduced into the point of the inner flame, where it should be held for two or three minutes before we conclude that it imparts no tint to the outer flame.

If two substances are found to platinum foil, in iron spoons, or glass reduction-tubes, it is usually with the intention of raising them to a high temperature without subjecting them to any chemical action of the flame: a broad-scattered blowpipe flame is generally used for this purpose, and is directed on to the bottom of the supports.

GLASSBLOWING.

§ 11. It is an important qualification of the practical chemist to be able to perform the simpler kinds of apparatus without the aid of the glassblower, since

¹ When reduction is made to employ as a flux, the loop should be wetted, in order that the reduction may advance more: it does not readily attach itself to the red-hot wire. When phosphorus salt is used it is advisable to give two turns to the wire in making the loop, and in giving the loop this twist to avoid, or at to form a sort of grating on which the heat conductive glass may be retained.

² This solution was in general prepared in the flame of the bulb derived from the burner in the apparatus, and should not touch the loop when once cleaned.

it not only effects a considerable saving of expense, but enables him to give to his instruments that form which suits his own taste; we shall here give a few brief directions, which may be useful in guiding the practice of the novice in this department.

Considerable difficulty is experienced in drawing and blowing glass before the mouth-blowpipe, and hence certain blowpipes are provided especially for this purpose. The chief of these are known as the table-blowpipe, Herapath's blowpipe, and the spirit-blowpipe, or, as it is commonly termed in the laboratory, the roarer.

The *table-blowpipe* is simply a table furnished with a lamp and blowpipe-jet, to which air is supplied from a pair of double-action bellows, worked by a treadle and weights beneath the table; the lamp is generally supplied with oil, and should have a good broad wick, which is kept well trimmed.

The *Herapath's blowpipe* consists of two brass tubes, one within the other, so contrived that when screwed on to the gas-pipe, a jet of gas may issue from the outer tube, and a stream of air may be forced from the mouth through a tube of vulcanized Indian-rubber, into the inner brass tube, which is terminated by a blowpipe-jet; the air is thus projected into the very centre of the gas-flame, and, the inner tube being made to slide up and down in the outer, the jet may be approached to, or withdrawn from the flame, so as to furnish a blowpipe-flame of any dimensions.

The *spirit-blowpipe-lamp* (*Rose's lamp*) is a sort of brass pot with double walls, into the interval between which a small brass tube penetrates nearly to the top, and enters the pot at the bottom, an inch above which it terminates in a pretty large blowpipe-jet; the space between the walls is about three-parts filled (through an aperture made for the purpose, and stopped either with the handle of the pot or with a good cork) with wood-naphtha, a small quantity of which is poured into the inside of the pot, so as to reach within about a quarter of an inch of the blowpipe aperture; if this be kindled, its flame heats the naphtha between the two walls, and converts it into vapor, which rushes out with a roaring noise through the jet, where it takes fire, thus producing a broad column of flame very well adapted for heating crucibles, drawing thick glass tubes, &c. It is scarcely necessary to observe that the naphtha poured into the space between the walls must be perfectly clear, for if any fragments of cork, &c. get into the blowpipe-aperture, the lamp may burst with considerable violence, and hence the dangerous reputation which these lamps have acquired; with a little care, however, they may be used with perfect safety, and are very valuable instruments, especially in laboratories where gas cannot be procured. If the jet of vapor should suddenly cease, the lamp must be immediately extinguished with the cover provided for this purpose.

The ordinary cases of working in glass which come under our notice in the laboratory, and which have not yet been referred to, are, the simple closure of tubes so as to preserve a uniform thickness, the sealing of tubes required to stand considerable internal pressure, the expansion into bulbs, the drawing out of tubes to a long open point, and the manufacture of the combustion-tubes used in organic analyses.¹

It is not difficult to close a tube so as to preserve a uniform thickness; a piece of tube is selected, about three inches longer than the required closed tube, and, having been first heated in the common flame (which precaution must be attended

¹ In manipulating with glass before the blowpipe, it should be observed, that the English glass is very liable to blacken, from the reduction of lead, and should therefore be heated only in the oxidizing flame, whilst the German glass may be exposed to the hottest part of the flame; in fact, for most purposes, the German glass is much superior to the English, and is always used when the tubes are required to bear a high temperature.

to in all glass-manipulations), at the point where the closing is to be effected, it is softened at about a quarter of an inch on each side of this point, by means of a coarse blowpipe flame, produced by the mouth-blowpipe, or by one of those especially devoted to glassblowing. The glass must be slowly turned round in the flame, as well as moved from side to side, so that it may be uniformly heated; when it is pretty soft, it is very gently drawn out in the flame by slowly separating the hands, the tube being still rotated, until the end is drawn off; at the end of the tube thus formed, there will be a little knob of fused glass, termed a *bleb*, which is removed by means of a piece of glass rod, first gently heated in the flame, so that the bleb may adhere to it. Hitherto, the tube has been held in the left hand; it is now shifted to the right, without removing it from the flame, and so turned that the whole of the closed extremity may be uniformly softened; when this is the case, the tube is quickly removed from the flame, and blown into with a steadily increasing pressure, which will have the effect of regularly expanding those portions of the glass which have been thickened in the flame, and thus, of equalizing its thickness. If great pressure be suddenly exerted upon the soft glass, it will be blown out into a very large thin bulb, which will immediately burst.

The *sealing of tubes* required to bear considerable pressure, is effected much in the same manner as the simple closure just described; but, in drawing off the end, it is retained in the blowpipe flame until it has acquired the necessary thickness, and no attempt need be made to take off the bleb.

In the manufacture of *glass bulbs*, the latter may be required at the extremity of the tube (as in thermometers), or in the middle (as in the tubes employed in reducing metallic oxides by hydrogen); for the former case, a piece of tube of the proper thickness having been selected (of course, the thicker the walls of the tube, the larger the bulb may be made), it is closed at one end, in the manner above described, and the bleb removed; the closed extremity is then well and uniformly softened in the flame, and retained there until the glass has acquired a thickness proportionate to the size of the required bulb; the tube is then rapidly removed from the flame, and a steadily increasing pressure applied by the mouth till the bulb is of the proper size; if this is not the case after a first attempt, the bulb must be uniformly reheated (which will cause it to collapse), and again expanded.

If the bulb is required on the body of the tube, one end of the latter, if not closed, must be stopped by a cork, the tube well softened regularly for about an inch, and then steadily expanded, as in the other cases; if the tube is rather thin, that portion upon which the bulb is required may be thickened, by gently pressing the tube, as it were, upon itself, when soft.

Tubes of moderate width, drawn out to a long open point, are often required in testing for arsenic. These are made by well softening about an inch and a half of the tube (German glass), then removing it from the flame, and rapidly but steadily drawing the ends apart, till the narrow tube thus produced is of about twice the required length, so that two arsenic-tubes may be obtained by one operation; they are then separated by a sharp file.

It is almost impossible to describe the manipulation requisite in drawing out the combustion-tubes for organic analysis, and none would be able to effect it after merely reading even the minutest description. The tube required is to be (of German glass) drawn out to a closed broad point, forming with the main tube an angle of about 45° , in such a manner that the section of the point in any part may be perfectly round, not flattened or elliptical; this is the result of a really difficult manipulation, which will be found to consist in forcibly drawing out the softened tube, with a peculiar turn of the wrist, which at once gives the proper angle, and preserves the roundness of the point.

ELEMENTARY CHEMISTRY.

§ 68. An element may be familiarly defined as a substance which cannot be resolved into anything further.

Our present elements are only the boundaries to which chemical research has hitherto penetrated; we have no evidence that some of these may not ultimately be shown to be compounds.

The number of elements at present discovered is sixty-four, of which only thirty-seven are ordinarily met with, the remainder being of comparatively rare occurrence, and, generally speaking, of little practical importance.

These sixty-four elements are divided into two classes; the *metals* and *non-metallic substances*, which latter are often improperly termed *metalloids*.

The distinctive features of these two classes are, in many cases, not very decidedly marked, and some chemists therefore place amongst the non-metallic bodies certain substances which others rank with the metals. A division like this, founded, in some cases, rather upon opinions than upon facts, may be looked upon as useful in affording assistance to the memory, but should not be considered one of the important features of the science.

We will state the chief points upon which this classification of the elements depends.

A *metal* usually possesses a peculiar power of reflecting light, which is denoted by the term metallic lustre, and it is a better conductor of heat and electricity than are non-metallic substances.

These are the chief physical differences; but it is in their chemical relations that the difference between these two classes of elements is most clearly perceived. The metals possess, generally, a great affinity for oxygen and the salt-radicals (chlorine, bromine, &c.), with which they combine to form, respectively, bases and salts; in fact, this property of forming a base by combination with oxygen, may be almost regarded as a *sine quâ non* in the definition of a metal, for there are few metals which do not exhibit it; whilst none of the non-metallic bodies are capable of forming basic oxides, and these latter are generally characterized by a tendency to form powerful acids by combination with oxygen.

It may then be generally asserted that all elements which possess a metallic lustre, which are pretty good conductors of heat and electricity, and which are capable of forming basic oxides, are *metals*, and that those elements which are not thus distinguished, are *non-metallic* substances.

The metals include by far the greater number of the elements, the non-metallic bodies numbering, according to the usual division, only thirteen; but of these twelve are of considerable importance, whilst twenty-five only of the metals receive any application worthy of notice in this work.

In the following list, the elements are enumerated, with their symbols and equivalents.

I. NON-METALLIC BODIES.

1. *Of considerable importance.*

BORON B	= 10.9	IODINE I	= 127.1
BROMINE Br	= 80	NITROGEN N	= 14
CARBON C	= 6	OXYGEN O	= 8
CHLORINE Cl	= 35.5	PHOSPHORUS P	= 32
FLUORINE F	= 18.9	SILICON Si	= 21.3
HYDROGEN H	= 1	SULPHUR S	= 16

2. *Of slight importance.*

SELENIUM Se = 39.5

II. METALS.

1. *Of considerable importance.*

ALUMINUM Al	= 13.7	MAGNESIUM Mg	= 12.2
ANTIMONY Sb	= 129	MANGANESE Mn	= 27.6
ARSENIC As	= 75	MERCURY Hg	= 100
BARIUM Ba	= 68.5	NICKEL Ni	= 29.6
BISMUTH Bi	= 213	PLATINUM Pt	= 98.7
CADMIUM Cd	= 56	POTASSIUM K	= 39.2
CALCIUM Ca	= 20	SILVER Ag	= 108.1
CHROMIUM Cr	= 26.7	SODIUM Na	= 23
COBALT Co	= 29.5	STRONTIUM Sr	= 43.8
COPPER Cu	= 31.7	TIN Sn	= 59
GOLD Au	= 197	URANIUM U	= 60
IRON Fe	= 28	ZINC Zn	= 32.6
LEAD Pb	= 103.7		

2. *Of slight importance.*

CERIUM Ce	= 47	PELOPIUM Pe	
DIDYMIUM D		RHODIUM R	= 52.2
ERBIUM E		RUTHENIUM Ru	= 52.2
GLUCINIUM Gl		TANTALUM Ta	= 184
ILMENIUM Il		TELLURIUM Te	= 64.2
IRIDIUM Ir	= 99	TERBIUM Tb	
LANTHANIUM La		THORIUM Th	= 59.0
LITHIUM Li	= 6.5	TITANIUM Ti	= 25
MOLYBDENUM Mo	= 46	TUNGSTEN W ¹	= 95
NIOBIUM Nb		VANADIUM V	= 68.6
OSMIUM Os	= 99.6	YTRIUM Y	
PALLADIUM Pd	= 53.3	ZIRCONIUM Zr	= 22.4

To these metals we must now add DONARIUM, which was discovered in the present year by Bergemann, in certain Norwegian minerals.

Another new metal, NORBIUM, also claims a place in the list.

Of the non-metallic elements, three, *oxygen, hydrogen, and nitrogen*, are permanent gases; and four, viz., *chlorine, bromine, iodine, and fluorine*, are known as the elementary salt-radicals.

From the mineral wolfram.

NON-METALLIC BODIES.

OXYGEN.¹

Sym. O. Eq. 8. Sp. Gr. 1.1057.

§ 69. OXYGEN was discovered by Priestley, in August, 1774, and one year later by Scheele, who was then unaware of Priestley's discovery.

Eighty-nine per cent. (by weight) of water consists of oxygen; atmospheric air also contains twenty-three per cent. of the same element, which likewise exists in combination with most of the other elements in various proportions.

Preparation.—The most important methods of preparing oxygen are:—

I. By heating binocide of manganese to redness in an iron retort (§ 28):—



II. By heating moderately in a flask, retort, or hard glass tube, a mixture of powdered chlorate of potassa with about one-fifth its weight of binocide of manganese. (The latter is not altered at the temperature employed, but by its presence considerably promotes the decomposition of the salt. Sand and sesquioxide of iron act in a similar manner, but with less energy.) The decomposition which chlorate of potassa undergoes, is shown by the following equation:—



The oxygen prepared from chlorate of potassa and binocide of manganese, almost always contains small quantities of chlorine, of carbonic acid, and of aqueous vapor. If required perfectly pure, it may be passed, first through a tube containing fragments of hydrate of potassa, which removes the two former impurities, and afterwards through a long bent tube containing pumice-stone, moistened with oil of vitriol, to remove the moisture (§ 28).

III. By heating the red oxide of mercury:—



IV. By heating together four parts of strong sulphuric acid, and three parts of bichromate of potassa:²—



§ 70. *Properties.*—Oxygen is a colorless, inodorous, and tasteless gas, which

¹ From *fluor*, acid, and *genia*, I produce.

² In heating chlorate of potassa by itself, if the process be arrested as soon as the evolution of gas begins to slacken, the salt will have undergone the decomposition represented by the following equation:—



When the heat is again continued, the evolution is renewed with increased violence, and the whole of the oxygen is evolved.

³ Bousingault has recently described a method of obtaining oxygen directly from the atmosphere, by passing a current of moist air over heated baryta (BaO), which is thus converted into binocide of barium (BaO_2); by exposing the latter, in the same apparatus, to an elevated temperature, the second equivalent of oxygen is again evolved, and may be collected as usual. This process has the advantage of being continuous, since the same amount of baryta may be made alternately to absorb and evolve an equivalent of oxygen.

has never yet been condensed to the solid or liquid form. It is very sparingly soluble in water. It supports combustion; any substance having considerable affinity for oxygen, on being introduced into it while undergoing combustion, burns with greatly increased brilliancy and rapidity.

If a piece of charcoal be attached to a copper wire, heated in the blowpipe-flame, and plunged with one point redhot into a jar of oxygen, it burns rapidly away, being converted into carbonic acid. Sulphur and phosphorus, kindled, and introduced into oxygen, also burn with great brilliancy (§ 33).

A chip of wood which has been kindled and blown out so as to leave a spark on the extremity, immediately bursts out into flame when immersed in a vessel of oxygen, thus affording a rough test of the quality of the gas.

Some substances (*e. g.* steel or iron wire), which only undergo gradual oxidation when exposed to the air, burn rapidly and brilliantly if introduced into oxygen, while in contact with some inflamed substance (§ 33).

Oxygen is indispensably necessary for supporting respiration; animal heat and life being dependent upon a gradual combustion (a slow combination of combustible substances with the oxygen inspired) in the system. This combustion would, however, proceed too rapidly, if pure oxygen were inhaled (arterial action being increased to an enormous degree). The atmosphere contains this element in a proper state of dilution for respiration.

Oxygen combines with all the elements (excepting fluorine); with many of them it unites in several proportions. Most of its combinations with metals have *basic* properties; those which it forms with metalloids are termed *acids* (§ 10).

Some few metallic oxides, consisting of three equivalents of oxygen to one of metal (*teroxides*), and others containing still more oxygen, possess feeble acid properties (*e. g.* antimonious and antimonie acids, SbO_2 & SbO_3 ; manganic and permanganic acids, MnO_2 & Mn_2O_7).

The name of oxygen was given by Lavoisier to this element, because at that time all known acids were believed to contain oxygen. At the present time we are well acquainted with a number of acids that contain no oxygen, and many circumstances tend to favor the view that hydrogen is the real acidifying principle.¹

§ 71. *Uses of Oxygen.*—Oxygen is sometimes used to accelerate combustion, thereby much augmenting the heat and light of certain flames: it has been applied to this purpose in the *Bude light*, in which the flame of the Argand lamp is supplied with oxygen. Substances which are with difficulty oxidizable are frequently submitted to the action of pure oxygen at a high temperature; this is especially the case in the incineration of certain organic substances.

§ 72. *OZONE.*²—This remarkable body was first discovered by Schönbein. He detected it in the atmosphere (by means of tests to be presently described), and found it to be formed in almost every instance of electric discharge into the air; also, when water is electrolyzed, and when phosphorus is allowed to act upon moist air at ordinary temperatures.

Preparation.—Ozone is best obtained by placing a piece of recently scraped phosphorus, about half an inch in length, into a clean bottle (of about two quarts capacity), in the bottom of which is as much water as will half cover the phosphorus; the mouth should then be closed slightly (to prevent any mischief ensuing if inflammation of the phosphorus should take place), and the bottle set aside. Ozone is almost immediately produced, its formation being indicated by the ascent of a column of vapor from the piece of phosphorus, and the luminosity

¹ Some interesting experiments recently made by Faraday have shown that oxygen is possessed of decided magnetic properties.

² ζ_{air}, to smell.

of the latter in the dark. Ozone may be detected in the bottle within a minute after the introduction of the phosphorus; if allowed to stand for six or eight hours, the air in the bottle will be abundantly charged with it. The phosphorus should then be removed, and the air freed from phosphorous acid by agitating some water in the bottle.

Properties.—The ozone thus obtained (in admixture with air) has the following properties: it is a colorless gas, possessing a very peculiar odor, which, when concentrated, much resembles that of chlorine, but when diluted is precisely the odor observed when an electric machine is in action. When air has been powerfully charged with ozone, it can be inspired with difficulty; it acts powerfully on the mucous membranes, producing very disagreeable sensations; small animals immersed in it soon cease to exist. Pure ozone must therefore be highly poisonous.

Ozone is insoluble in water; it possesses powerful bleaching properties, and also acts as an energetic oxidizing agent, transforming phosphorus into phosphoric acid, and powerfully oxidizing many metals, converting them and their lower oxides into the highest oxides they are capable of forming. Thus, lead and silver are converted into oxides, antimony and arsenic into arsenic acid and antimonic acid; the salts of the protoxides of manganese, cobalt, nickel, are decomposed by it, the acids being evolved and the binoxides formed. It also decomposes many hydrogen-acids (*e. g.* hydrosulphuric acid), and oxidizes organic compounds. It combines with chlorine, bromine, and iodine, and is in many respects analogous in its action to the binoxide of hydrogen.

Two views are entertained respecting the constitution of this body; the one, that it is oxygen in an allotropic condition—the other, that it is a compound of oxygen similar to binoxide of hydrogen. The former is the view which possesses the greater number of supporters, particularly since it has been proved that, on passing dry ozonized air through a redhot tube, the destruction of ozone by the heat (it being only capable of forming at ordinary temperatures) is unaccompanied by the production of any water.¹ Many organic compounds, such as ether and turpentine, when exposed to the action of air and light, undergo peculiar changes, and acquire very powerful bleaching and oxidizing properties, apparently by association with ozone.

Tests for Ozone.—The most delicate test for the presence of ozone is prepared in the following manner: one part of pure iodide of potassium and ten parts of starch are boiled together, for a few moments, with two hundred parts of water, and white filtering-paper is saturated with the liquid thus obtained. Such paper is immediately turned blue when introduced moist into ozonized air. If introduced dry it will remain colorless, but becomes blue immediately upon being moistened.

Paper prepared with a solution of sulphate of manganese is also a good test for ozone, becoming rapidly brown from formation of binoxide when introduced into ozonized air.

¹ By very recent researches, Baumert believes that he has shown the ozone obtained in the electrolysis of water to consist of a teroxide of hydrogen. He passed the perfectly dry ozone, first through a tube containing anhydrous phosphoric acid, which was unaffected by it, then through a tube heated to redness, and lastly, through a second tube, containing phosphoric acid, which indicated the presence of moisture produced in the decomposition of the ozone. The proportion of oxygen was determined by passing the ozone into a standard solution of iodide of potassium.

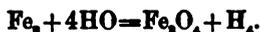
HYDROGEN.¹

Sym. H. Eq. 1. Sp. Gr. 0.0692.

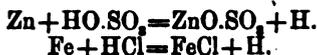
§ 73. **HYDROGEN** was discovered by Cavendish, in 1766. It constitutes 11 per cent. by weight of water; it also occupies an important place in the composition of nearly all organic substances.

Preparation.—Hydrogen may be prepared:—

I. By passing the vapor of water through an iron tube filled with iron nails, and heated to redness:—



II. By adding dilute sulphuric acid (or hydrochloric acid) to granulated zinc (or fragments of iron), covered with water, in a Woulfe's (or common wide-mouthed) bottle provided with a funnel-tube and delivery-tube (§ 27):—



The gas may be collected over water (§ 29) or by upward displacement (§ 31):—

III. By decomposing water with potassium or sodium, in a small jar filled with mercury, and standing over the mercurial trough:—



IV. By heating zinc or iron with solution of potassa, when the oxygen of the water is abstracted by the metal.

In experiments with hydrogen, the operator must allow the gas to be evolved for two or three minutes without attempting to collect it, so that all the atmospheric air may be expelled from the apparatus, since the neglect of this precaution may be attended with danger from the formation of an explosive mixture.

The hydrogen prepared with commercial zinc or iron is never pure. It has a nauseous odor due to a peculiar compound of hydrogen with carbon derived from the metal; small quantities of sulphur and arsenic are also obtained from the same source, and pass off in combination with hydrogen (arsenic is also sometimes derived from the oil of vitriol). In order to purify this gas, it should be passed first through solution of potassa; secondly, through solution of nitrate of silver, and lastly, if the gas be required free from aqueous vapor, through a bent tube containing pumice-stone moistened with oil of vitriol, or through a wash bottle, containing this liquid (§ 28). It is difficult to dry hydrogen perfectly, on account of its high diffusive power (§ 22).

§ 74. *Properties.*—Hydrogen is a permanent gas, colorless, and, if quite pure, inodorous. Its solubility in water is somewhat less than that of oxygen. This gas is the lightest substance known; its lightness may be readily shown by pouring it upwards from one jar into another, each jar being afterwards presented to the flame. Hydrogen is a very inflammable gas; if a lighted taper be thrust up into an inverted jar of hydrogen, the taper is extinguished, but the gas takes fire at the mouth of the jar, and burns with a pale bluish flame. If hydrogen, dried by means of chloride of calcium, be burnt at a glass jet (§ 32), and a dry jar held over the flame, the water which is produced in the combustion will be observed to condense upon the glass.

The flame of hydrogen, though very faintly luminous, has a very high temperature.

If a jet of hydrogen be burnt in a long wide glass tube, open at both ends, the vibrations, caused by the alternate extinction and rekindling of the flame, succeed each other so rapidly as to produce a musical tone.

¹ *Edup, water, yowda, I produce.*

The diffusive power (§ 22) of hydrogen is exceedingly high, whence it can be preserved only in vessels which are very tightly closed with stoppers.

OXIDES OF HYDROGEN.

Water HO.

Binoxide of Hydrogen, HO₂.

WATER, HO. *Eq. 9. Sp. Gr. 1.*

§ 75. A mixture of two volumes of hydrogen and one volume of oxygen explodes, when brought in contact with flame, when suddenly and powerfully compressed, or when an electric spark is passed through it, producing water, which, in the state of vapor, at 60° F. and 30 inches bar. would occupy two volumes.

On introducing spongy platinum or finely divided platinum (platinum-black) into a mixture of the gases, it is instantly exploded. Or, if a jet of hydrogen be allowed to impinge upon a ball of spongy platinum in the air, the metal will become redhot, and the hydrogen will be immediately afterwards ignited. Faraday has shown that the union of the two gases may be even effected by a perfectly clean surface of rolled platinum. This remarkable property of platinum¹ led Döbereiner to the construction of his beautiful little apparatus for the production of instantaneous light. Various opinions are entertained respecting the manner in which spongy platinum acts in effecting the combination of hydrogen with oxygen. Platinum, in a finely divided state, has been found to possess the remarkable property of condensing in its pores about 253 times its volume of oxygen, whereby the latter must be rendered even denser than water. It has been supposed that hydrogen, coming in contact with oxygen in this highly condensed state, combines with it immediately. Another view taken by some chemists of this phenomenon is based upon the supposition that when finely-divided platinum is exposed to air or oxygen, it becomes covered, even at the common temperature, with a very minute coating of oxide, which is reduced to metal again by hydrogen, even in the cold. It is therefore supposed that, when the oxygen of the air and a jet of hydrogen are allowed to act upon spongy platinum, a series of continuous oxidations and reductions takes place, accompanied by a rise in temperature sufficient to heat the platinum to redness, and thereby to set fire to the hydrogen.

A mixture of hydrogen and oxygen in proper proportions may also be exploded in an eudiometer, by the electric spark (§ 32). They then combine with a sudden flash, and without noise, water being produced.

The combination of hydrogen and oxygen is accompanied by the disengagement of the most intense heat that can be produced. If the mixed gases are allowed to issue under some pressure from a narrow jet, and inflamed, the heat disengaged by the combustion is sufficiently powerful to melt platinum and pipe-clay, which substances resist the heat of all furnaces. The flame of this jet of mixed gases (generally termed the *oxyhydrogen-blowpipe* jet) is very pale, but becomes dazzling the moment a solid infusible substance is introduced into it. Thus, if the flame be allowed to fall upon a disk of lime, a star of most intense light is obtained, which is generally known by the name of the *Drummond* or *lime-light*. This phenomenon is owing to the state of intense incandescence of the particles of lime when exposed to the heat of the oxyhydrogen flame. Various forms of apparatus have been contrived to supply the jet with the mixed gases.

¹ Other substances besides platinum, such as gold, palladium, and even some stones and glass, possess this property to some extent, requiring, however, the aid of heat to effect the combination.

The safest are those in which the gases are retained in separate reservoirs, and only allowed to mix in small quantities, just as they are to be burnt, that portion of the apparatus between the jet and the chamber in which the mixture is effected being stuffed with very thin brass wires, by which means, owing to the conducting power of the metal, the temperature is so far reduced that all danger of explosion is avoided (*Hemming's jet*).

§ 76. THE COMPOSITION OF WATER may be ascertained in various ways.

I. *By Synthesis*.—If a mixture of two volumes of hydrogen and one of oxygen is detonated in an eudiometer, as just now mentioned, the gases will disappear entirely, water being formed. Again, if a current of dry and pure hydrogen be passed over a known amount of pure and thoroughly-dried black oxide of copper in a bulb-tube, to which a gentle heat is applied, the oxide will be reduced to the metallic state, water being formed, which may be collected by attaching a chloride of calcium tube, previously weighed, to the extremity of the bulb-tube, the latter being kept hot, in order to prevent the condensation of the water until it arrives at the chloride of calcium tube. After the copper is perfectly reduced, it may be weighed; the loss will represent the oxygen which has combined with the hydrogen; the increase of weight of the chloride of calcium tube will give the amount of water produced in the experiment.

II. *By Analysis*.—The decomposition of water by the galvanic current may be also resorted to for demonstrating its composition.

If the current is allowed to pass through acidulated water contained in a glass vessel, the poles of the battery being terminated by platinum-plates, which are introduced into the bottom of the latter in such a manner that they pass up a little way into separate graduated tubes, in which the gas is collected as it is generated at each pole, it will be found that the tube over the negative pole is filled with gas, while that over the positive pole is only half-filled (the dimensions of the tubes being alike); upon examination of the gas, that evolved at the positive pole will be found to be pure oxygen, while that collected at the negative pole is hydrogen (§ 17).

This experiment proves, therefore, that water consists of 1 volume of oxygen to 2 of hydrogen; and by calculation from the known specific gravities of these gases, this proportion will be found equal to 1 by weight of hydrogen, and 8 of oxygen.

§ 77. *Properties of Water*.—At ordinary temperatures (of warm and temperate climates), water is, when pure, a colorless, tasteless, and inodorous liquid. It solidifies to ice or snow at 32° F. (0° C.) It may, however, when perfectly tranquil, be cooled down to a temperature far below the freezing point, without solidifying, but if then agitated in the slightest degree, it will instantly become a solid mass, the temperature simultaneously rising to 32° F. Ice belongs in form to the hexagonal system of crystals. Snow also appears in regular hexagonal tables, and in groups of these, more or less elongated, and united in the form of a star. The specific gravity of ice is 0.9184. It is a remarkable circumstance that water, unlike other liquids, contracts when cooled beyond a certain point, and attains its maximum density at 39.2° F. (4° C.) If, therefore, a mass of water is exposed to air having the temperature of its freezing point, the upper layer will sink as it cools, until the above point of maximum density is attained, after which contraction will no longer take place, and consequently the surface will be covered with a coating of ice, which protects the rest of the liquid from further refrigeration; and herein we may perceive an admirable provision of nature for the preservation of the inhabitants of the waters during severe winters, besides the many other most important results arising from the expansion of the freezing water, such, for instance, as the disintegration of rocks, &c.

When impure water freezes, the ice which separates is generally free from impurities; thus, when sea-water is exposed to a very low temperature, crystals

of nearly pure ice are deposited, the salts remaining in the mother-liquor. Gases dissolved in water also separate when the latter is frozen, and remain imprisoned in the ice in the form of minute bubbles.

Ice is transparent and colorless, and a bad conductor of heat. At temperatures above 32° F. (0° C.) it melts into water; the latter boils at 212° F. (100° C.)¹ being converted into an invisible vapor (*steam*).²

The specific gravity of aqueous vapor is 0.622, 100 cubic inches weighing, at 212° F. (100° C.) 14.96 grains.³

In the state of vapor, water occupies 1700 times the space which it does at ordinary temperatures in its liquid state. Water is but slightly compressible. It vaporizes at all temperatures, even when in the state of ice, in the coldest climes; hence aqueous vapor is continually ascending into the air from the surface of the earth, to which it returns when condensed, in the form of dew, rain, hail, snow, or rime (hoar-frost).

Water is a perfectly neutral body; yet it combines with a great number of substances, forming what are termed *hydrates*. With chlorine and bromine, and with these *elements* only, it forms hydrates, containing 10 atoms of water. It also combines with acids and with bases, forming hydrates which correspond generally in their composition to the neutral salts of these substances; it therefore occupies, at times, the place of a base, and at others that of an acid.

With neutral salts, water enters into combination in two different conditions; first, as water of crystallization, which is easily expelled by heat; secondly, as saline or constitutional water, which is more difficult to separate from the salt (§ 21).

Water possesses the property of dissolving the greater number of substances, acting almost invariably as a simple solvent. By this means solids are converted into the liquid state; this property of water is of the highest importance to chemists, enabling them to effect with ease chemical changes which would otherwise be accomplished with difficulty.

The solvent power of water is much increased by an elevation of temperature, as we have already noticed, and this is also the case with steam; the solvent action of water at high temperatures is economically applied, in the apparatus known as *Papin's digester*, to the extraction of nutritious portions of animal food.

§ 78. Water cannot occur pure in nature, on account of its solvent property. *Rain*, which is the purest kind of water, always contains carbonate and nitrate of ammonia. *Spring-waters* are contaminated to a greater or less extent with various salts, which are extracted from the earth, such as carbonate of lime (chalk), sulphate of lime (gypsum), chloride of sodium, and other alkaline salts. Much carbonate of lime is frequently held in solution in water by free carbonic acid, which forms with it a bicarbonate. When such waters are boiled, the carbonic acid is expelled, and the carbonate of lime precipitated in the crystalline form, together with a certain amount of sulphate of lime and sesquioxide of iron, forming a very hard incrustation on the bottoms of steam-boilers, the safety of which is often thus endangered.

¹ Grove has found that water is resolved into its elements at very high temperatures. The extremity of a platinum wire was fused into a small button, afterwards raised to a temperature approaching its fusing point by the oxyhydrogen blowpipe, and then suddenly plunged into water; a mixture of oxygen and hydrogen was immediately evolved. Aqueous vapor was also decomposed by passing it through a platinum tube heated to whiteness, and by the influence of electric sparks passing from pole to pole.

² The white clouds of steam formed when aqueous vapor of considerable tension escapes into the atmosphere, should be distinguished as *vesicular vapor*, since it consists of a number of vesicles formed by minute drops of water, and distended by true aqueous vapor.

³ It must be remembered that the standard with which the specific gravities of vapors are compared is that of dry atmospheric air at 60° F. (§ 1.)

This incrustation may be, to a certain extent, prevented by various means; the best and safest chemical process is that proposed by Ritterbrandt, which consists in the addition of chloride of ammonium to the water in the boiler. The carbonic acid is expelled from the water as carbonate of ammonia, while the lime is held in solution as the highly soluble chloride of calcium. Chloride of tin has lately been recommended for the same purpose. Alkaline carbonates are also found to prevent the incrustation of boilers.

The remarks above applied to spring-waters will suffice for those of *rivers*; we have only to add that the latter, in the neighborhood of large towns, are often much contaminated with organic matters, and the nitrates and salts of ammonia derived therefrom.

Waters containing much earthy impurity are termed *hard*, while purer waters are called *soft*. The former are more agreeable to the taste than the latter, but give rise to the production of insoluble salts (of lime and magnesia), with the fatty acid of the soap, and are hence less applicable to detergent purposes. Various methods have been suggested for reducing the hardness of spring and river waters; the most simple and efficacious is that proposed by Clark, which consists in adding to the water an amount of solution of lime sufficient to form carbonate of lime with the free carbonic acid; the carbonate originally held in solution in the water is thus precipitated, together with the newly formed chalk. (For a mode of testing the hardness of water, see Quantitative Analysis; special methods.)

Waters containing foreign matters in solution, to such an extent as to have a peculiar taste or smell, or to acquire medicinal properties, are termed *mineral* waters. Of these, there are several kinds; *saline* waters are such as contain neutral salts in considerable quantity, such as sulphate of magnesia (Epsom salts), chloride of sodium, &c. The waters of Cheltenham afford good examples of saline waters. Waters containing much iron are termed *chalybeate*. (In these the iron is held in solution as carbonate of the oxide of iron, by free carbonic acid; upon allowing such waters to stand, or on boiling them, the iron is deposited as sesquioxide.) Those waters containing much hydrosulphuric acid (sulphuretted hydrogen), or free carbonic acid, are termed *sulphurous*, *carbonated*, or *acidulous* waters. Examples of the former are the Harrogate; of the latter, the Pymont and Seltzer waters.

Sea-water is peculiarly rich in saline constituents, the chief of which are chlorides of sodium and magnesium, sulphates of magnesia and lime, and traces of bromides and iodides.

Distillation is the method universally employed for purifying water from solid matter (§ 38).

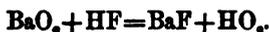
It becomes difficult to obtain perfectly pure water even by this means, since water exercises its solvent action upon most metals, and even upon glass. The following special precautions should be attended to in the distillation of water. The head of the still should be of sufficient height to preclude the possibility of any of the contents splashing into the worm, which should not be made of lead or iron, but rather of tin, copper, or silver. If chloride of magnesium exists in the water, some lime should be added previously to distillation, since that salt is decomposed by protracted ebullition with water, into magnesia and hydrochloric acid, which latter would pass over into the distillate if the above precaution were not adopted.

When it is desired to have water perfectly free from gases, it must be boiled for some time, and then immediately bottled up closely, since it absorbs air by mere exposure in open vessels. For the action of water upon lead, see the history of lead.

BINOXIDE OF HYDROGEN, OR OXYGENATED WATER.

HO₂. Eq. 17.

§ 79. This compound, which was discovered by Thénard, in 1818, is formed when certain metallic binoxides, such as binoxide of barium (which is always employed for this purpose), are digested with dilute acid (*e. g.* hydrofluoric acid) at a low temperature, when the change will be represented by the following equation:—



This substance having received at present no practical application, we shall not enter more minutely into detail respecting its preparation, which requires many precautions.

Properties.—Binoxide of hydrogen is a colorless, transparent, syrupy liquid; its taste is harsh, bitter, and astringent, something like that of tartar-emetic.

It does not freeze at -22°F. (-30°C.), and evaporates without decomposition at ordinary temperatures; it does not redden litmus, but gradually bleaches both turmeric and litmus; it whitens the tongue, and also the cuticle when placed on the hand, producing violent itching after a time.

Binoxide of hydrogen retains the second atom of oxygen in a very loose state of combination. It escapes from the water under various circumstances; sometimes so rapidly as to cause violent effervescence, evolution of heat, and even explosion, accompanied at times by a flash of light. The decomposition is effected by contact of the binoxide with carbon, binoxide of manganese, and various other metallic oxides, by several metals, and also by heat. Some oxides, in effecting its decomposition, are reduced to the metallic state, or to a lower state of oxidation (oxides of gold, silver, mercury, &c., and the red and brown peroxides of lead). No reasonable explanation can be given of these singular reactions.

Binoxide of hydrogen is miscible with water in all proportions, and also combines with the hydrated acids, with which it forms compounds in which it is less easily decomposable than when uncombined.

NITROGEN¹

Sym. N. Eq. 14. Sp. Gr. 0.972.

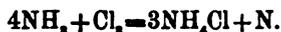
§ 80. Nitrogen was discovered by Rutherford, in 1772.

The atmosphere contains about 77 per cent. by weight, or 79 per cent. by volume, of nitrogen. This element is also an important constituent of animals and vegetables. It occurs, though not abundantly, in the mineral kingdom.

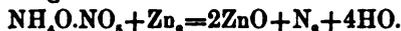
Preparation.—I. Nitrogen may be obtained by abstracting the oxygen from atmospheric air; this is effected by burning some phosphorus or sulphur in air, confined over water, under a bell-jar; the resulting sulphurous or phosphoric acid may be removed by washing the gas, which then consists of pure nitrogen. (The washing may be effected by cautiously transferring the gas from one jar to another, through water.)

Nitrogen may be also obtained,

II. By passing chlorine into a solution of ammonia:—



III. By heating a strong solution of nitrate of ammonia with granulated zinc:—



¹ *Nitron*, nitre, and *γενάω*, I produce.

IV. By heating a mixture of nitrite of potassa and chloride of ammonium :—



The first and fourth methods only are in general use in the laboratory.

Properties.—Nitrogen is a permanent gas, devoid of color, taste, and smell, and not possessing any active properties. It is incombustible, and does not support combustion; it consequently will not support respiration. It is, however, not poisonous in its properties, since, when mixed with oxygen, it may be breathed with impunity; in fact, we have seen above, that $\frac{1}{4}$ of the bulk of the atmosphere consists of nitrogen.

It therefore plays an important part in diluting oxygen so as to render it fit for continuous respiration. This gas is much less soluble in water than oxygen.

Nitrogen does not enter into direct combination with any elements excepting oxygen, with which it may be made to unite by subjecting the mixture of the gases to a succession of powerful electric sparks.

It may be obtained in combination with most non-metallic elements, and with a few metals. Thus, we have chloride, iodide, bromide, and carbide of nitrogen, and nitrides of iron and copper. The most important compounds of nitrogen are those which it forms with hydrogen and oxygen. It combines with the latter in five different proportions, forming nitrous oxide (NO), nitric oxide (NO_2), nitrous acid (NO_2), peroxide of nitrogen (NO_4), and nitric acid (NO_5).

With hydrogen, it produces the substance ammonia (NH_3), besides which, three other compounds of nitrogen and hydrogen are assumed, though they have not yet been isolated—namely, ammonium NH_4 , amidogen NH_2 , and imidogen NH .

OXIDES OF NITROGEN.

Protoxide of Nitrogen . . .	NO	Peroxide of Nitrogen . . .	NO_4
Binoxide of Nitrogen . . .	NO_2	Nitric acid	NO_5
Nitrous acid	NO_2		

PROTOXIDE OF NITROGEN, NITROUS OXIDE, LAUGHING-GAS.

NO . *Eq. 22. Sp. Gr. 1.524.*

Composition by Volume.—Two volumes of this gas contain two volumes of nitrogen and one volume of oxygen.

§ 81. *Preparation.*—Nitrous oxide is prepared by heating moderately in a glass retort the nitrate of ammonia (§ 23, *et seq.*).

This salt is decomposed by heat into nitrous oxide and water :—



The application of heat should be gradual, and the temperature not raised too high, as in that case a portion of the salt volatilizes undecomposed, and a violent explosion may likewise occur. Care must be taken that the salt be free from chloride of ammonium, or the gas obtained will be contaminated with chlorine.

The protoxide may also be obtained by dissolving zinc in very dilute nitric acid, or by the action of chloride of tin upon nitromuriatic acid: the best method is to introduce, gradually, crystals of nitre, or small cylinders of fused nitre, into a strongly acid solution of chloride of tin, heated in a water-bath. The most convenient apparatus for this operation is a wide-necked generating-flask, fitted with an upright tube, dipping into the solution of tin, and sufficiently wide to admit of the gradual introduction of the nitre.¹

¹ It has been lately proposed to prepare nitrous oxide by heating sal-ammoniac with moderately strong nitric acid.

Protoxide of nitrogen must be collected over mercury or warm water, being soluble in cold water.

Properties.—Nitrous oxide is a colorless gas, possessing a sweet taste. By exposure to a pressure of about 50 atmospheres, at a temperature of 45° F. (7° C.), it is converted into a colorless mobile liquid, producing a wound like a burn when placed upon the hand. This liquid may be solidified by exposure to the cold of a carbonic-acid bath *in vacuo* (about -150° F., -100° C.), a white mass being obtained, which melts in the hands, and evaporates suddenly, blistering the skin. The gas does not burn, but supports combustion, inflamed substances burning in it with increased energy. Phosphorus, when fully kindled, and plunged into the gas, burns in it with great brilliancy.

It does not affect vegetable colors, being an indifferent body. It may be inhaled for a short time, producing very singular effects, resembling in many respects those of intoxication. The sensations experienced by persons inspiring the gas are in most cases of an agreeable kind; the effects very frequently are, increased muscular action and an irresistible inclination to laugh. Such effects only last for two or three minutes, and, in most cases, are not followed by depression of spirits or exhaustion, but on the contrary, by increased liveliness, even for some time after the gas has been inhaled. Sometimes, however, the inhalation of the gas is followed by disagreeable symptoms, even to loss of consciousness.¹ This singular property of nitrous oxide was first discovered by Sir H. Davy. On immersing animals in nitrous oxide, they become very restless, and expire after some time.

A mixture of nitrous oxide with an equal volume of hydrogen, explodes when inflamed, water being formed, and nitrogen liberated. A certain quantity of ammonia is also produced. Platinum-black becomes redhot in the mixture, likewise effecting the above change.

Nitrous oxide is soluble to a considerable extent in cold water, one volume of the latter absorbs about 0.7 or 0.8 of the gas, which is evolved again upon boiling. The aqueous solution has a sweetish taste.

When passed through a redhot porcelain tube, this gas is decomposed, yielding a mixture of nitrogen, oxygen, and binoxide of nitrogen.

BINOXIDE OF NITROGEN, NITRIC OXIDE.

NO₂. Eq. 80. Sp. Gr. 1.0416.

Composition by Volume.—1 volume of oxygen to 1 volume of nitrogen without condensation.

§ 82. *Preparation.*—Nitric oxide is prepared by dissolving copper in moderately strong nitric acid (spec. grav. 1.2), in a small apparatus similar to that employed for preparing hydrogen:—



It may also be obtained by heating mercury, lead, or silver, with nitric acid.

If the nitric acid is employed too concentrated, the gas is frequently contaminated with nitrogen. It may be collected over cold water, which absorbs only from $\frac{1}{5}$ to $\frac{1}{7}$ of its bulk of the gas.²

Properties.—Nitric oxide is a colorless gas, which has not been liquefied; the moment it comes in contact with air, it combines with oxygen, forming yellowish-

¹ The best apparatus for administering laughing-gas is a capacious bladder, provided with a wooden mouthpiece, having a lateral opening, which may be closed by the thumb of the operator until the state of the patient renders the admission of air necessary.

² Nitric oxide may also, like the protoxide of nitrogen, be prepared by the action of chloride of iron upon nitro-muriatic acid, or upon fragments of nitre, in the presence of free hydrochloric acid, as described at § 81.

red vapors of peroxide of nitrogen (NO_2). Its smell and taste cannot therefore be ascertained. It is not combustible, and supports the combustion of only a few substances (*e. g.* burning phosphorus). It can only be resolved into its elements at a very high temperature. It cannot be breathed in a pure state. It does not affect litmus, being a neutral body, and is copiously absorbed by a solution of protosulphate of iron, producing a brown liquid, from which the greater portion of the gas may be expelled again by continued boiling.

The formation of hyponitric acid from nitric oxide, by contact with oxygen, forms an excellent test for the latter gas in a free state.

One volume of sulphurous acid, when mixed with two of nitric oxide, in the presence of water, is slowly converted into sulphuric acid, nitrous oxide being formed:—



A mixture of equal volumes of hydrogen and nitric oxide, when inflamed in the air, burns with a greenish-white flame, yielding hyponitric acid vapor, the hydrogen appearing to unite with oxygen from the atmosphere only.

Iron, and a few other easily oxidizable metals, if retained in contact with nitric oxide, reduce it gradually to protoxide of nitrogen; but if the gas be passed into water containing the binoxides of manganese or lead in suspension, the *nitrites* of the oxides of these metals are formed: by the action of nitric oxide under similar circumstances upon oxide of silver, nitrite of silver and metallic silver are obtained.

If two or three drops of bisulphide of carbon be poured into a jar of nitric oxide, well agitated therein, and afterwards inflamed, the mixture emits a bright blue luminous flash.

TEROXIDE OF NITROGEN, NITROUS ACID, HYPONITROUS ACID.

NO_2 . Eq. 38.

§ 83. *Preparation.*—This compound is produced when nitric oxide is brought in contact with air, in the presence of potassa (or another strong base), the nitrite of potassa being formed.

It is also produced by passing dry nitric oxide through anhydrous hyponitric acid, or by thoroughly mixing one volume of oxygen and rather more than two volumes of nitric oxide, and cooling the mixed gases down to -4°F. (-20°C.) The best method of producing it, is to heat in a capacious retort one part of starch with eight parts of nitric acid, of spec. grav. 1.25, and to pass the gaseous product through a long chloride of calcium tube, and then through an U-tube, cooled down to -4°F. (-20°C.)

Properties.—Nitrous acid, when pure, is a highly volatile liquid, of a blue color, which boils below 32°F. ; its vapor has a yellowish-red color. When distilled, it undergoes partial decomposition, being reconverted into nitric oxide and hyponitric acid:—



It dissolves in water at 32°F. (0°C.) without decomposition, yielding a light blue solution, which, at temperatures above 32°F. , evolves a large quantity of nitric oxide, nitric acid remaining in solution in the water:—



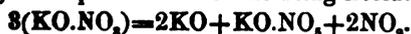
Nitrous acid combines with many bases, forming nitrites; some of these may be obtained by heating the nitrates. Thus, when nitrate of potassa is fused and kept for some time at a red heat, it parts first with two atoms of oxygen, forming nitrite of potassa, which, by continued heating, is converted into caustic potassa.

The nitrate operated upon should therefore be heated until a portion dissolved in water gives a slight alkaline reaction, and affords, with nitrate of silver, a

pale-brown precipitate, which consists of nitrate of silver mixed with a little oxide, which imparts to it the faint brown color.

Nitrites are either white or light yellow, and most of them may be crystallized.

An aqueous solution of a nitrite, when boiled for some time, is converted into nitrate, nitric oxide, and a portion of the base being liberated:—



HYPONITRIC ACID, PEROXIDE OF NITROGEN, NITROUS ACID.

NO_2 . Eq. 46.

Composition by Volume.—2 volumes of the gas contain 1 volume of nitrogen and two volumes of oxygen.

Preparation.—This acid is formed when nitric oxide is mixed with oxygen or atmospheric air; one volume of dry oxygen is mixed with nearly two volumes of perfectly dry nitric oxide, and passed through a tube cooled down to -4°F . (-20°C).

Or dry nitrate of lead is submitted to distillation in a retort with which a cooled reservoir is connected (§ 39):—



Properties.—Peroxide of nitrogen is obtained, according to the above directions, as a liquid, which is colorless at -4°F . (-20°C), but on the temperature rising, becomes first pale-yellow and afterwards orange-yellow. It crystallizes at about -4°F . in colorless prisms, and melts again at $15^\circ.8 \text{F}$. (-9°C .) It boils at about 82°F . (28°C .), yielding a dark yellowish-red vapor, which becomes apparently nearly black when further heated.

This vapor is scarcely condensable when mixed with air or other gases; hence hyponitric acid was formerly believed to be a permanent gas. It has a sweetish but pungent and suffocating odor, and an acid taste. It reddens litmus, and imparts a yellow stain to animal matters.

Peroxide of nitrogen is decomposed by most oxidizable metals, as copper, tin, mercury, sodium, and potassium, the latter taking fire in it, and burning with a red flame. Water decomposes it, nitric acid and binoxide of nitrogen being produced:—



If the quantity of water present is small, the products of decomposition are nitrous acid and nitric acid:—



The peroxide of nitrogen was formerly termed nitrous acid, but it is decomposed by the alkaline bases, giving rise to nitrates and nitrites.

NITRIC ACID.

NO_3 (*anhydrous*) or *hydrated acid*, $\text{HO}.\text{NO}_3$. Eq. 54.

§ 85. Nitric acid occurs in nature, in combination with potassa, soda, lime, and magnesia (particularly with the two first named, with which it forms *nitre* and *cubic nitre*). In some hot climates, such as those of India and Peru, these salts form incrustations of considerable thickness on the surface of the soil. Nitric acid is also found in the water of some springs and rivers in the neighborhood of populous towns, in rain water after thunderstorms, and in some plants, which absorb it from the soil.

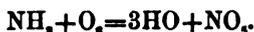
ANHYDROUS NITRIC ACID, NO_3 , has been recently discovered by Deville, who succeeded in obtaining it by passing a very slow current of chlorine, first over chloride of calcium and sulphuric acid, and afterwards over well-dried nitrate of

silver, previously heated to 203° F. (95° C.), and then maintained at a temperature of 136° to 150.8 F. (56° to 66° C.) The products are passed into a U-tube, cooled down to 5°.8 F. (-21° C.) Oxygen escapes, and crystals of nitric acid are obtained, besides a volatile liquid, probably nitrous acid.

Properties.—Deville describes anhydrous nitric acid as a substance crystallizing in brilliant colorless rhombic prisms, which fuse at 84.2 to 86° F. (29° to 30° C.) It boils at 113° to 122° F. (45° to 50° C.), and is decomposed at about that temperature. When brought into contact with water, it dissolves with considerable evolution of heat, hydrated nitric acid being formed.

HYDRATED NITRIC ACID, HO.NO₃.

§ 86. Nitric acid is formed in *nitre-heaps*, by the spontaneous decomposition of nitrogenous animal matter in the presence of bases. Ammonia is first disengaged, and this appears to be gradually converted by the oxygen of the air and contact with porous bodies, into nitric acid and water, the former combining with the base to form a nitrate:—



Nitric acid is likewise formed by the action of the electric spark upon a mixture of nitrogen and oxygen, in the presence of water, and is most probably produced in this manner during thunderstorms. Ammonia also yields nitric acid when exposed to the action of oxidizing agents under certain circumstances.

Preparation.—Hydrated nitric acid is prepared by distilling a mixture of equal parts by weight of hydrated sulphuric acid (oil of vitriol) and nitrate of potassa. The distillation is conducted in a glass retort, the neck of which should be rather long, and is passed at once into the cooled receiver. No cork or lute may be used (§ 40). Since the nitre of commerce generally contains some chloride of potassium or sodium,¹ the first portion of acid that passes over contains chlorine, and should therefore be rejected.

The above proportions correspond nearly to one equivalent of nitre and two of hydrated sulphuric acid (1 equivalent of nitre=101, 2 equivalents of sulphuric acid=98; a slight excess of acid is advantageous). The decomposition which the nitre undergoes is represented by the following equation:—



Nitric acid is also obtained if one equivalent only of sulphuric acid is employed. A much higher temperature is, however, then required, by which a portion of the nitric acid is decomposed, being converted into oxygen and peroxide of nitrogen. The latter is absorbed by the nitric acid, imparting to it a brownish color.² The bisulphate of potassa is also far more readily removed from the retort than the neutral sulphate produced in the latter case, on account of its greater fusibility and solubility.

Nitrate of soda is sometimes used instead of nitrate of potassa, and is generally employed for the manufacture of this acid on the large scale (one equivalent of the salt being used, to one of hydrated sulphuric acid).

The distillation of nitric acid on the large scale is effected in horizontal cast-iron cylinders. In order to insure the purity of nitric acid (which, if the first portion be collected separately, will be nearly free from chlorine, but may contain sulphuric acid and small quantities of fixed salts), it should be redistilled with the addition of a small quantity of nitre. (Tests for the purity of nitric acid, *see Analysis, Reagents.*) To obtain nitric acid perfectly free from chlorine, it may be mixed

¹ A very simple method of expelling the chlorine from nitre consists in stirring it at a gentle heat, with a few drops of nitric acid, till a specimen dissolved in water no longer gives a turbidity with nitrate of silver.

² If the acid be required colorless, it may be rendered so by gently heating it until all peroxide of nitrogen is expelled.

with an excess of nitrate of silver and redistilled. The best method of obtaining very concentrated nitric acid, is to distil the ordinary acid with two parts of oil of vitriol, at a temperature not exceeding 284° to 302° F. (140° to 150° C.)

Properties.—Hydrated nitric acid is a colorless liquid when pure, giving off dense grayish-white fumes on exposure to damp air, in consequence of the formation of a less volatile hydrate. The strongest acid has a specific gravity of 1.522; it freezes at a temperature between —40° and —65°.2 F. (—40° and —51° C.), yielding a mass like butter. Hydrated acid of the highest specific gravity begins to boil at about 108° F. (42° C.), the boiling-point gradually rising as the acid becomes weaker (a portion being decomposed into peroxide of nitrogen and oxygen), until the temperature has reached 248° F. (120° C.), when an acid of the spec. grav. 1.42 (having the formula $\text{HO}\cdot\text{NO}_2 + 3\text{HO}$, and containing 60 per cent. of NO_2), is obtained. If, on the other hand, an acid weaker than this last be distilled, the boiling-point gradually rises to 248° (water, with a little acid, passing over), and the acid of spec. grav. 1.42 then distils over, so that this acid is the constant product of the distillation of hydrated nitric acid of any strength.

Hydrated nitric acid has a pungent characteristic odor, and is very acid and corrosive, destroying organic matter or staining it yellow. It possesses a considerable affinity for water, which it attracts from the atmosphere; when the strong acid is mixed with water much heat is evolved. Snow, when mixed with moderately strong nitric acid (sp. gr. 1.4), liquefies instantly, intense cold being produced.

Hydrated nitric acid undergoes decomposition with considerable facility. When its vapor is passed through a redhot porcelain tube, it is decomposed into nitrogen and oxygen, or peroxide of nitrogen and oxygen, according to the temperature employed. It undergoes decomposition by mere exposure to the light, becoming yellow. In consequence of the feeble manner in which nitric acid retains a portion of its oxygen, it is a most powerful oxidizing agent, acting upon all oxidizable substances with more or less violence. These oxidations are generally attended by evolution of heat, which in some instances is so great as to inflame the substance acted upon. Thus, phosphorus thrown into the strongest nitric acid inflames, and is converted into phosphoric acid; oil of turpentine, and some other essential oils, are also inflamed when mixed with the strongest nitric acid. Small pieces of redhot charcoal, thrown into strong nitric acid, continue to glow with increased brilliancy.

Lower oxides are converted into higher by nitric acid, and most metals are first oxidized and then dissolved. The very strongest nitric acid has no action upon many metals, such as iron and lead, but when slightly diluted it oxidizes them powerfully. When metals are exposed to the oxidizing action of nitric acid, the latter loses one, three, and sometimes five equivalents of oxygen; and in the case of those metals which decompose water in the presence of acids (as tin and zinc), ammonia is also formed.

Nitric acid combines with basic oxides to form nitrates, most of which are neutral, their composition being represented by the formula $\text{MO}\cdot\text{NO}_2$. There are also some basic nitrates containing a larger proportion of base to the acid than that above given.

Nitrates are decomposed by heat; in some cases oxygen is at first liberated, the nitrites being formed, which are decomposed by continued application of heat; in other cases the acid is decomposed into peroxide of nitrogen and oxygen.

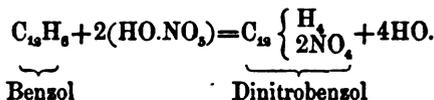
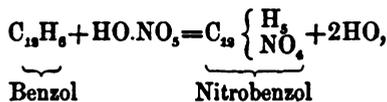
Nitrates are also decomposed by sulphuric acid, and mostly deflagrate when thrown upon ignited charcoal.

The action of nitric acid upon organic substances consists either in a simple conversion of the substance into products of oxidation, or merely in the oxidation of one or more equivalents of hydrogen, which are replaced by an equivalent

quantity of peroxide of nitrogen (NO_2). An example of the first kind of action is the conversion of oxalic acid into carbonic acid:—



The second kind of action is illustrated by the production of *nitrobenzol*, and *dinitrobenzol* from *benzol*, which is represented in the following equations:—



FUMING NITRIC ACID is, properly speaking, a mixture of very strong nitric acid with peroxide of nitrogen. It is a red liquid, evolving yellowish red fumes on exposure to the air. Fuming nitric acid is turned green by addition of a small quantity of water, nitric oxide being evolved; a large quantity of water destroys the color.

*Uses of Nitric Acid.*⁴—The oxidizing and solvent powers of nitric acid render it a highly valuable agent in the hands of the chemist.

In combination with potassa, it is largely used in the manufacture of gunpowder and also in fireworks. It is also used in dyeing, for the production of yellow patterns upon a colored ground. The dilute acid is employed in lithography. Nitric acid is occasionally used in medicine, and also as a fumigating agent, its fumes being less irritating than those of chlorine. For this purpose pounded nitre and sulphuric acid are heated together in an open vessel. Certain vegetable substances when acted upon by this acid, yield highly explosive compounds. This property has of late been applied to the manufacture of *gun-cotton*, *gun-paper*, &c.

ATMOSPHERIC AIR.

Sp. Gr. 1. 100 cubic inches weigh 31.0117 grs.

§ 87. The air which constitutes our atmosphere consists of a mechanical mixture of oxygen and nitrogen, containing small and variable quantities of aqueous vapor, carbonic acid, and traces of a few other substances both inorganic and organic. The property possessed by gases of becoming intimately and thoroughly mixed, however much they may differ in their density, or, in other words, the diffusion of gases, accounts for the great uniformity of this mechanical mixture in different parts of the atmosphere.

Oxygen and nitrogen are present in the atmosphere in the proportion of about two equivalents of the latter to one of the former; 100 volumes of air contain 79.19 nitrogen, and 20.81 oxygen. By weight, the proportions are 77 nitrogen, and 23 oxygen.

Numerous methods have been resorted to for determining the proportions of oxygen and nitrogen in atmospheric air. The branch of chemistry to which such operations belong is termed eudiometry, and has already been referred to, and the apparatus employed therein described (§ 32). Volta's method is that most

⁴ The impure nitric acid of commerce is known by the name of *aqua fortis*: its spec. grav. ranges from 1.4 to 1.5, and it generally contains hydrochloric and sulphuric acids as impurities.

The *nitrous acid* of commerce consists of nitric acid containing NO_2 , and is usually prepared by distilling nitrate of potassa with half its weight of sulphuric acid.

generally adopted for determining the amount of oxygen. A certain volume of air is confined in an eudiometer over water or mercury, and mixed with about half its bulk of pure hydrogen; a second measurement is then made, and the mixture afterwards exploded by the electric spark (§ 32). The gaseous residue in the tube, after detonation, consists of nitrogen and the excess of hydrogen; this is measured, and the amount deducted from the volume before the explosion; the result divided by three, gives the amount of oxygen contained in the air, since the whole of that element will have combined with the hydrogen to form water, and the latter consists of one volume of oxygen to two of hydrogen. The oxygen is sometimes determined by introducing a stick or ball of phosphorus, attached to a fine iron wire, into a measured portion of air confined over water.

If this arrangement be allowed to remain for about twenty-four hours in a warm place, the phosphorus undergoes slow combustion, being converted into phosphorous acid, which is absorbed by the water, while nitrogen only remains in the tube. Oxygen may also be estimated in a variety of ways by means of substances, principally in the liquid state, having a powerful affinity for oxygen, which they abstract from air at ordinary temperatures. Thus, Sir H. Davy recommended for this purpose, a solution of sulphate of iron saturated with nitric oxide; a solution of a salt of the suboxide of copper in ammonia is also frequently used, and Liebig has not long since discovered that an alkaline solution of pyrogallic acid absorbs oxygen rapidly from the air, and is the most convenient reagent for effecting its analysis. Another most accurate method of analyzing air, is to allow a quantity to flow into an exhausted glass globe (of known weight), first passing through a series of tubes containing, respectively, potassa and concentrated sulphuric acid, and then through a weighed tube filled with bright copper turnings, and heated to redness in a charcoal fire. The increase in the weight of the latter tube, owing to the oxidation of the copper, gives the amount of oxygen corresponding to the nitrogen weighed in the globe.

§ 88. The following is a short account of the foreign matters existing in the atmosphere.

Aqueous Vapor.—The quantity of aqueous vapor existing in air is very variable, depending much on the temperature; its presence is highly essential to animal and vegetable life; perfectly dry air would soon prove fatal both to plants and animals. The presence of water in the atmosphere is easily demonstrated, by exposing some deliquescent substance (such as fused chloride of calcium) to the air; the moisture will soon be attracted, and after a time the chloride will become quite liquid.

Various instruments have been constructed for the determination of moisture present in the atmosphere, which are termed *hygrometers*.

That most generally approved of has been contrived by Daniell (usually known as the *wet-bulb* hygrometer). Another method of determining the water is that of Brunner, which consists in drawing a measured quantity of air, by means of an aspirator, through a weighed tube containing asbestos moistened with strong sulphuric acid, and ascertaining the increase in the weight of the tube.

Carbonic Acid.—This gas is always present to a small extent in air (according to Marchand, 3.1 in 1000), being derived from the processes of combustion and respiration. The carbonic acid thus constantly produced, is to a great extent removed from the air by plants, to the existence of which it is essential, since they assimilate its carbon, and restore the oxygen to the air.

The amount of this gas present in air may be ascertained by drawing air as above directed, first through a drying tube, and then through another tube with two divisions, containing hydrate of potassa in the first, and some asbestos moistened with sulphuric acid in the second division (to absorb any moisture carried away from the hydrate of potassa). The increase in weight of this tube will give the amount of carbonic acid.

Ammonia.—This impurity in the atmosphere is generated by the putrefaction of nitrogenized organic substances; though it may be distinctly detected in air, and particularly in rain water (by which it is absorbed from the atmosphere), its quantity is very inconsiderable. It is absorbed in a remarkable manner by some substances when exposed to the air. Thus, sesquioxide of iron, or white clay, previously ignited, will be found when heated after protracted exposure to the air, to evolve considerable quantities of ammonia.

Besides the above impurities, a few others are at times to be detected in the air or in rain-water, particularly in the neighborhood of large towns; the chief of these is hydrosulphuric acid. Certain organic matters are also contained in the air. It is supposed that the contagious matter of several epidemic diseases exists in the form of an organic poison disseminated through the atmosphere, and to which the name of *miasma* has been given. *Marsh-gas* is also an impurity found in the air in the neighborhood of stagnant waters, or in coal-mines, where it forms the highly dangerous *fire-damp*.

The average composition of the air is always the same, since a most simple and beautiful balance is kept up in nature between animal and vegetable respiration. As already stated, the oxygen consumed in the production of carbonic acid by combustion in air or respiration of animals, is continually restored to the atmosphere by the plants, which retain for their own nourishment the carbon, to serve again as support for animal life.

The constitution of atmospheric air was for a long time matter of dispute; it is now, however, generally believed to be a mechanical mixture of oxygen and nitrogen, the constant composition of which may be accounted for by reference to the law of diffusion, and by a consideration of the slight difference in the specific gravities of its component gases.

The following arguments may be cited in support of this view:—

1. The composition by volume of atmospheric air would be anomalous, if it were a combination of nitrogen and oxygen.
2. The properties of air are such as would be predicted of a mere mechanical mixture of the two gases.
3. A mixture of nitrogen and oxygen in proper proportions exhibits all the properties of atmospheric air, without our perceiving any of the phenomena usually attendant upon chemical combination.
4. Water, exposed to air, absorbs each gas in the same proportion as if it were in a perfectly free state.

NITROGEN AND HYDROGEN.



Those inclosed in brackets are hypothetical.

AMIDOGEN, NH₂=Ad. *Eq.* 16.

§ 89. We are not acquainted with this body in a separate state; we have, however, very good reasons for assuming its existence in many compounds.

When potassium and sodium are heated in ammoniacal gas, it will be found that one-third of the hydrogen escapes; the residue has the composition KNH₂, or NaNH₂:—



This compound is termed *amidide*, or *amide of potassium*.

When certain metallic chlorides are mixed with aqueous ammonia, compound amides are also produced:—



A far larger number of amides exist in organic chemistry, consisting of amidegen in combination with some other complex atoms. When brought into contact with water in the presence of acids or alkalies, they are resolved into ammonia and oxidized products.

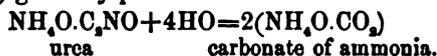
AMMONIA.

NH_3 . Eq. 17. Sp. Gr. 0.5902.

Composition by Volume.—1 volume of nitrogen and 3 volumes of hydrogen combine to form 2 volumes of ammonia.

§ 90. Ammonia occurs in the air as carbonate of ammonia; in some rivers, springs, and mineral waters, as chloride of ammonium, or some other salt. The rock-salt of the Tyrol contains chloride of ammonium (sal-ammoniac); sesquioxide of iron and aluminous or ferruginous rocks, after exposure to air, yield ammonia when heated; some plants contain salts of ammonia; it is also found in one or two minerals of recent formation, and in animal secretions.

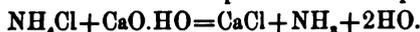
When a mixture of 2 volumes of nitric oxide and 5 volumes of hydrogen is passed over spongy platinum, or other porous substances (heated to redness), ammonia and water are produced. The quantity formed by exposing a mixture of nitrogen and hydrogen gases to the action of an electric current is very minute; but if hydrogen, at the moment of its liberation, meet under certain circumstances with nitrogen, ammonia will be produced. In the rusting (oxidation) of iron by water containing atmospheric air, ammonia is formed in this manner. Most nitrogenized organic substances yield ammonia, either by dry distillation, or by heating with an alkali. Animal secretions yield ammonia in abundance, when allowed to undergo fermentation or putrefaction. Thus, in urine, the urea (cyanate of ammonia) gradually passes over into carbonate of ammonia:—



Large quantities of ammonia are also obtained in the distillation of coal (for the preparation of gas) and of bones; and from these sources most of the ammonia of commerce is at present obtained.

Carbonate of ammonia was first extensively prepared from camels' dung, in Egypt.

Preparation.—The best mode of preparing dry ammonia in the laboratory, is to heat gradually in a retort or flask, a mixture of 1 part of chloride of ammonium, and 2 parts of hydrate of lime, allowing the gas to pass first into a small bottle with a safety-tube, in which any moisture may be to a great extent condensed, and afterwards through a tube filled with fragments of quicklime, to complete the desiccation of the gas, which must either be collected over mercury, or by upward displacement in inverted vessels, it being considerably lighter than air. The production of ammonia in this process is thus represented:—



Properties.—Ammonia is a colorless gas, of a peculiar and exceedingly pungent odor; it does not support combustion, but a jet of the gas burns with a yellow flame in an atmosphere of oxygen. When inspired pure, it is fatal to animals. It is converted by a pressure of six and a half atmospheres at 50° F. (10° C.) into a colorless, mobile liquid, the spec. grav. of which is 0.76; gaseous ammonia is likewise transformed at a very low temperature, into a colorless, translucent, crystalline solid, which melts at -113° F. (-75° C.) Liquid ammonia may be obtained by heating some chloride of silver saturated with gaseous ammonia, in one arm of a sealed tube of tough glass (such as recommended by Faraday for the liquefaction of gases), and surrounding the other arm with ice; the ammonia will be evolved, and condensed by its own pressure

in the cold extremity of the tube. On allowing the chloride to cool, the ammonia is again absorbed by it; the heat evolved by this recombination raises the temperature of the chloride of silver to 100°.4 F. (38° C.); while the other end of the tube in which the ammonia was condensed, becomes very cold.

Ammonia is powerfully alkaline; when brought into contact with hydrogen-acids, or with hydrated oxygen-acids, it produces ammoniacal salts; and hence volatile acids, such as hydrochloric, nitric, and acetic, are often used as a test for gaseous ammonia, with which the vapors of these acids produce white clouds.

If a flask filled with ammoniacal gas be opened under water, the latter rushes in with great rapidity, in consequence of the absorption which takes place.

SOLUTION OF AMMONIA, LIQUOR AMMONIÆ.

Water absorbs nearly half its weight (or about 670 times its volume) of ammoniacal gas. A solution of this description constitutes the *aqua ammoniæ fortissima* of commerce.

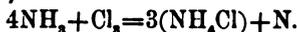
It is prepared by connecting a glass or earthenware vessel, charged with the above-mentioned mixture for the preparation of ammonia (slightly moistened with water), with three Woulfe's bottles, fitted with safety-tubes; the first containing but little water, the second, an amount about equal to the weight of chloride of ammonium employed, and the third, a smaller quantity.

The gas is washed in the first bottle (the first portion being also absorbed), the water in the second bottle then becomes gradually saturated with pure ammoniacal gas; that in the third retains any ammonia that may escape absorption in the second bottle. These bottles should be kept cool by being surrounded with cold water.

Properties.—The solution of ammonia is colourless. It varies in *spec. grav.* from nearly 1.000 to 0.850, according to its strength. (The strongest ammonia of commerce has a *spec. grav.* of about 0.87). It does not freeze until between —36° and —42° F. (—38° —41° C.) It possesses the peculiar odor of the gas, and a sharp burning taste. The greater portion of ammonia is expelled from its solution below 212° F. (100° C.)

Solution of ammonia is most extensively used by chemists, being a highly important reagent. It is also employed medicinally, for which purpose it is diluted to the *spec. grav.* 0.96.

Dry ammoniacal gas, when submitted to the electric spark, is resolved into 3 volumes of hydrogen and 1 of nitrogen; ammonia may be also decomposed by contact with highly heated platinum, copper or iron,¹ and by detonation with oxygen. Chlorine gas decomposes it rapidly at ordinary temperatures, yielding nitrogen gas and hydrochloric acid; the latter, combining with another portion of ammonia, forms chloride of ammonium; an excess of chlorine produces chloride of nitrogen (§ 97).



This action is at times accompanied by the production of a flash of light. Ammoniacal gas is also decomposed under various circumstances, and with more or less rapidity, by some of the oxides of nitrogen (particularly hyponitric acid), by some metallic oxides, &c.

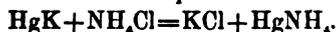
AMMONIUM, NH₄. Eq. 18.

§ 91. This compound has never yet been isolated; numerous observations,

¹ It has been very recently shown that ammonia is resolved into its elements at a temperature far below redness, when passed through tubes containing heated quicklime. It has even been proposed to employ this method for the preparation of hydrogen free from arsenic, &c., when the presence of nitrogen is not objectionable.

however, have led chemists to believe that it exists, and is in its properties similar to a metal.

If a galvanic current is allowed to act upon a solution of an ammoniacal salt, the end of the negative pole dipping into mercury, the latter is observed to increase gradually in bulk to a considerable extent, becoming of the consistency of butter, and at the same time retaining its metallic lustre. By placing an amalgam of potassium or sodium on a piece of moistened chloride of ammonium, or in a solution of the latter, the same compound is produced. This is regarded as the amalgam of mercury with the substance ammonium, NH_4 . When it is placed in water, the mercury returns to its original state, hydrogen and ammonia being evolved. The increase in weight which the mercury exhibits when converted into the amalgam, is very trifling. The decomposition of potassium-amalgam by chloride of ammonium is represented as follows:—



The assumption of the existence of the compound metal, ammonium, based upon this and other experiments, furnishes us with a very simple view respecting the constitution of the ammoniacal salts.

Ammonia was formerly believed to combine directly with hydrogen-acids and also with oxygen-acids. The composition of the hydracid salts is in accordance with this view, since they may be represented by the general formula, NH_3HR ;¹ it is most probable, however, that if an oxygen-acid unites (as it sometimes does) directly with NH_3 , it does not form a true salt, but that the presence of an equivalent of water is indispensably necessary to the production of a salt of ammonia with an oxygen-acid. This difference in the behavior of ammonia with the two classes of acids is not easily explained, unless we adopt the view of Berzelius in assuming the existence of the substance ammonium, NH_4 .

Ammonia + 1 eq. of water, $\text{NH}_3 + \text{HO}$, must then be viewed as $\text{NH}_4\text{O} = \text{AmO}$, the oxide of ammonium, analogous to KO , the oxide of potassium or potassa; this oxide then unites with oxygen-acids to form salts of the oxide of ammonium, such as $\text{NH}_4\text{O}\cdot\text{SO}_3$ or $\text{AmO}\cdot\text{SO}_3$; NH_4HCl , the hydrochlorate of ammonia, must in this case be viewed as NH_4Cl , or AmCl , chloride of ammonium, analogous to chloride of potassium. An analogy between the salts of ammonia, and those of the alkalies to which they are, in many respects, so similar, cannot be traced by the first mode of viewing their composition; but as soon as we assume the existence of ammonium, the most striking analogy is, as we have shown, exhibited between the composition of the salts of ammonia and of potassa or soda; the main difference consisting in the point, that $\text{Am}(\text{NH}_4)$ is a compound, while K and Na are elements; several analogous cases are, however, to be found in chemistry, in which a compound body, the chemical or physical properties of which are indeed perfectly well known, comports itself towards other bodies exactly like certain elements; and, indeed, most chemists are far from maintaining the impossibility of a future discovery that some of the present elements are compound bodies (§ 101).

Various objections have been raised to the ammonium-theory of Berzelius, and other theories have also been advanced; the above is, however, the most simple, and hence is most generally adopted by chemists.

¹ R representing the radical of the hydrogen-acid.

CHLORINE.¹

Sym. Cl. Eq. 35.50. Sp. Gr. 2.44.

§ 93. Scheele discovered chlorine in 1774. Gay-Lussac and Thénard were, however, the first to class it among the simple bodies in 1809. Its elementary character was afterwards fully established by Davy.

Chlorine occurs in combination in many mineral substances, such as rock-salt (chloride of sodium), also in sea-water and marine plants, as chlorides of sodium and potassium.

Preparation.—Chlorine is obtained:—

I. By gently heating in a flask, binoxide of manganese with strong hydrochloric acid:—



II. By heating a mixture of binoxide of manganese, chloride of sodium, and moderately dilute sulphuric acid:—



When chlorine is required perfectly dry, it should be passed through concentrated sulphuric acid.

The gas may be collected either by downward displacement (§ 31), or if required perfectly free from atmospheric air, over water, the delivery-tube being passed to the top of the gas-jars.¹

Properties.—Chlorine is a yellowish-green gas, of a pungent suffocating odour; it is incombustible, and supports the combustion of a few bodies for which it has an affinity. Some elements, such as arsenic and phosphorus, inflame spontaneously in chlorine, as also certain compounds rich in hydrogen, such as ammonia and oil of turpentine; a wax taper continues to burn for some time in this gas, with deposition of carbon, the hydrogen of the wax combining with the chlorine which has a more powerful affinity for that element. Chlorine is incapable of supporting respiration, causing instantaneous death when inhaled pure; when breathed in small quantities, it causes cough and sneezing, accompanied by an oppressive and choking sensation in the chest, sometimes followed by spitting of blood. When light is directed on max. however, be administered, to allow

It may be condensed to a pressure of about four atmospheres as a yellow liquid (sp. gr. 1.48).

Chlorine expands when mixed, discharges vegetable odours. It also possesses the remarkable property of destroying vegetable odours and infectious matters.

One volume of water in the presence of chlorine. It rises when dry chlorine is introduced, it appears to absorb hydrogen directly from the substance, thereby rendering the water dry some degrees of moisture only. But if water is present, and more chlorine be added, must have equal than the dry gas, its hydrogen is now gradually abstracted by the chlorine, and the liberated oxygen will speedily combine with either dissolving it entirely, or converting it into some volatile and infectious matter.

Water dissolves about one volume of chlorine gas at ordinary temperatures. The solution may be prepared by passing a slow current of chlorine

into cold water.

Ammonia has a remarkable affinity for the absorption of chlorine, when the solution is exposed to the atmosphere. It has a dry mixture of ammonia and chlorine, which is sometimes used as a disinfectant, and is a rapid

through water, until the latter is saturated.) It has the color, odor, and bleaching properties of the gas, and must be preserved in the dark in small bottles, perfectly filled and well stoppered, as it is liable to decompose on exposure to light (into hydrochloric acid and oxygen).¹

Chlorine has extremely powerful affinities for some metalloids, and for most metals. In combination with nitrogen, it forms a highly explosive liquid, chloride of nitrogen; it combines with hydrogen to form hydrochloric acid. Oxygen unites with it in several proportions (though not directly, under any circumstances), producing hypochlorous acid (ClO), chlorous acid (ClO₂), peroxide of chlorine (ClO₂), chloric acid (ClO₃), perchloric acid (ClO₇).

Chlorine also forms one or two compounds with carbon. It combines with most metals, forming chlorides of various compositions, corresponding in most cases with their oxides.

Uses of Chlorine.—Immense advantage has been derived from the use of chlorine as a bleaching agent. In bleaching by the old process, by exposure to the sun and air, a large surface of ground was required, and long exposure was necessary, from which considerable damage to the fabrics resulted.

The chief modes of applying chlorine as a bleaching agent are: the *retort-bleaching*, in which the moist gas is employed, and the use of bleaching-powder (chloride of lime), of which more will be said hereafter. The latter substance is also generally used as a source of chlorine when this gas is employed as a disinfectant; if the chloride of lime be mixed into a paste with water, and sulphuric acid added from time to time, a regular evolution of chlorine is maintained.

CHLORINE AND OXYGEN.

Hypochlorous acid . . . ClO	Chloric acid ClO ₃
Chlorous acid ClO ₂	Perchloric acid . . . ClO ₇
Peroxide of Chlorine . ClO ₂	

HYPOCHLOROUS ACID, ClO. Eq. 43.5.

Composition by Volume.—2 volumes of chlorine and 1 volume of oxygen form 2 volumes of hypochlorous acid.

§ 94. *Preparation.*—This acid is produced by diffusing finely-divided red oxide of mercury through about twelve times its weight of water, which is introduced into a bottle containing chlorine gas, and agitated therein till the latter is absorbed. A solution of hypochlorous acid is thus obtained, together with an oxychloride of mercury:—²



The oxychloride of mercury is removed by subsidence, and the weak solution obtained, introduced into a small flask, which is then heated in the water-bath, and the evolved gas conducted into a smaller portion of water, when a pure solution of ClO is obtained; afterwards, the gas may be evolved from this solution by introducing a few fragments of some highly deliquescent salt, such as chloride of calcium, or nitrate of lime; but the experiment is attended with considerable danger. The gas may be obtained in the anhydrous state by passing dry chlorine over red oxide of mercury in a tube surrounded with a freezing mixture. The gas disengaged is collected over mercury in bottles provided with tight and

¹ When cooled nearly to the freezing point, the solution of chlorine deposits yellow crystals of *hydrate of chlorine*, Cl+10HO, which Faraday employed in order to obtain the gas in a liquid state.

² The solution of hypochlorous acid thus obtained generally contains chloride of mercury.

greased stoppers. Hypochlorous acid must not be allowed to remain long in contact with mercury, since the latter gradually decomposes it.

Properties.—Hypochlorous acid is a deep yellow gas, possessing a very powerful penetrating odor. It may be liquefied by passing the dry gas into a U-tube, cooled down to a temperature of -4° F. (-20° C.) When exposed to a gentle heat, or brought into contact with some combustible bodies (white unsized paper, for example), it explodes, yielding two volumes of chlorine and one volume of oxygen. It rapidly decomposes many organic substances. It is easily absorbed by water, the latter taking up about 100 times its own volume. The solution has a pale yellow color, and possesses powerful bleaching properties, and the peculiar odor of the gas. It is not acid to test-papers, and is easily decomposed by light, and by organic substances having affinities for chlorine or oxygen.

The combinations of this acid with bases are termed *hypochlorites*. The so-called *chlorides* of the alkalis, or alkaline earths (the bleaching salts), consist of a mixture of chloride of the metal with the hypochlorite of the base. They are prepared by passing chlorine into water containing the bases, or their carbonates, dissolved or in suspension; the temperature being kept low during the operation. The decomposition may be expressed as follows:—



It is to be observed that this decomposition only takes place when cold dilute solutions of the bases are employed; if these be hot or concentrated, no hypochlorite is formed, but instead, a chlorate and chloride:—



Hypochlorites may be distinguished from the bleaching salts by their comportment with acids. The former yield hypochlorous acid, the latter chlorine, when treated with an acid:—



The hypochlorites have a peculiar astringent taste; they consist of 1 eq. of base to 1 eq. of acid.

Their solutions, as well as those of the bleaching salts, undergo gradual decomposition at ordinary temperatures. When boiled, they are converted into chlorates and chlorides:—



The hypochlorites possess bleaching properties, but the most powerful action is produced by adding an acid to the chlorides of lime, &c., since, as we have just seen, chlorine is evolved. Hypochlorites have the power of converting low metallic oxides, such as the oxides of lead and manganese, into higher oxides.

The chlorides of soda and lime are used most extensively, as bleaching and disinfecting agents, in the manner above described. Their oxidizing action upon certain organic substances is also accompanied by the production of beautiful though transient colors, which afford the chemist suitable means for testing for such compounds.

EUCHLORINE.—This gas was first described by Sir H. Davy, in 1811. It is evolved when 1 part of chlorate of potassa is heated with two parts of hydrochloric acid and 2 of water. It has a bright yellow color, a smell similar in some respects to chlorine, though peculiarly sweet, and possesses bleaching properties. It contains chlorine and oxygen in the proportion of their equivalents, like hypochlorous acid, but has been pretty clearly proved to be a *mixture* of chlorine and peroxide of chlorine. The most remarkable circumstance connected with the formation of this gas, is, that it always consists of the same proportions

of its elements. The following equation may explain the decomposition of chlorate of potassa by hydrochloric acid:—



CHLOROUS ACID, ClO_2 . *Eq.* 59.5. *Sp. Gr.* 2.646.

§ 95. This acid is produced by heating a mixture of chlorate of potassa and nitric acid with some deoxidizing agent (such as arsenious acid). Its formation seems to be the result of the action of nitrous acid, produced by the deoxidation of nitric acid, upon the chloric acid:—



Properties.—Chlorous acid is a dark greenish-yellow gas, possessing a pungent odor and bleaching properties. It may be condensed to a red liquid by exposure to intense cold.

When heated to 135° F. (57° C.) it explodes, being resolved into chlorine and oxygen. Contact with combustible substances likewise causes it to explode.

Water dissolves about six times its volume of the gas; the color of the solution varies from green to yellow according to its degree of saturation. It possesses bleaching properties, and exerts an oxidizing action on many of the lower metallic oxides. Chlorous acid combines with bases to form *chlorites*, some of which are crystallizable. It is expelled from its combinations by carbonic acid.

PEROXIDE OF CHLORINE, HYPOCHLORIC ACID, ClO_4 . *Eq.* 67.5.

Sp. Gr. 2.338.

Preparation.—Finely powdered chlorate of potassa is very gradually mixed into a paste with strong sulphuric acid, and gently heated in a bath containing a mixture of alcohol and water. A yellow gas is disengaged, which must be cautiously collected by downward displacement, or over mercury, upon which, however, it acts considerably. The greatest care must be taken not to raise the temperature too high, or explosion will immediately ensue; it is, indeed, advisable for the operator to wear an iron wire mask. The chlorate of potassa employed should be as pure and dry as possible, since the presence of water or chloride of potassium greatly increases the risk of explosion. The decomposition is expressed by the following equation:—



Properties.—Peroxide of chlorine is a yellow gas, of rather brighter color than chlorine, and a somewhat aromatic smell. It destroys the color of moist litmus paper. The gas may be converted by pressure at 0° F. (−18° C.) into a deep yellow, mobile, transparent fluid, which evaporates rapidly on exposure to air, and is highly explosive. Peroxide of chlorine is easily decomposed, either by exposure to light, by heat, or by the electric spark. It also explodes violently if brought into contact with sulphur or phosphorus. It is somewhat soluble in water; the solution is rapidly decomposed on exposure to sunlight. Water also forms a solid hydrate when poured upon the liquid peroxide of chlorine at 32° F. (0° C.)

When brought into contact with an alkali, peroxide of chlorine appears to be converted into chloric and chlorous acids:—



and hence the existence of this substance as an independent acid is much doubted.

CHLORIC ACID, ClO_3 (*anhydrous*). *Eq.* 75.5.

This acid is produced by boiling the solution of a hypochlorite; or by passing

chlorine into a hot concentrated solution of an alkali. Hypochlorous acid is first produced:—



which is subsequently decomposed as follows:—



Properties.—Chloric acid has not been obtained in the anhydrous state; its concentrated solution (obtained by adding an equivalent proportion of sulphuric acid to chlorate of baryta, and submitting the decanted liquid to spontaneous evaporation *in vacuo*) is colorless, and has highly acid properties; it has an oily appearance and a pungent smell; paper dropped into it takes fire; it is decomposed at temperatures above 104° F. (40° C.); when boiled it is converted into perchloric acid, chlorine, and oxygen:—



Chloric acid is not decomposed by light; its oxidizing properties are very powerful.

The compounds of chloric acid with bases, called *chlorates*, are decomposed by heat; in most cases the oxygen contained in the salt is evolved, metallic chlorides remaining behind.

When mixed with combustible substances, such as phosphorus, sulphur, sugar, antimony, arsenic, &c. chlorates explode, frequently with great violence, either by friction, or by the application of heat; in these cases the combustible substances extract the oxygen, which is in a state of but feeble combination with the chlorine. Chlorates are decomposed by concentrated sulphuric acid, the chloric acid being converted into perchloric and hypochloric acids, with disengagement of chlorine and oxygen. The decomposition is attended by decrepitation and the disengagement of heat, frequently so considerable as to produce detonation and flashes of light. A mixture of chlorate of potassa with an equal bulk of sugar inflames when brought into contact with a small quantity of oil of vitriol.

Chlorates are also decomposed by nitric acid, the chloric acid being converted into peroxide of chlorine, chlorine, and oxygen. Hydrochloric acid, when added to a chlorate, evolves, as just now stated, a yellow gas known by the name of euchlorine.

The chlorates are soluble in water; some of them to such an extent as to be deliquescent. Their solutions have no action on vegetable colors, unless mixed with a free acid, when a bleaching property is imparted to them by the decomposition of the salt.

Uses of Chlorates.—Chloric acid in the free state has met with no application, on account of the difficulties attending its preparation in any considerable quantity; the explosive property of chlorates when mixed with combustible substances has been turned to considerable advantage in the preparation of detonating mixtures, chlorate of potassa being the salt most generally employed. This salt, mixed with phosphorus, sulphur, &c. forms the principal mixture for the preparation of lucifer matches.



Millon has found that by passing euchlorine through several U-tubes surrounded by freezing mixtures, a red liquid was condensed, resembling liquid peroxide of chlorine; it is soluble in water, boils at about 89.6° F. (32° C.), and does not explode below a temperature of 158° F. (70° C.) Like peroxide of chlorine, it yields a chlorate and a chlorite when treated with potassa; the proportions of the salts formed are, however, 2 eqs. of chlorate to 1 of chlorite. Hence, he assigns to this acid the above composition.

PERCHLORIC ACID, ClO_7 Eq. 91.5.

Preparation.—This acid is produced when chloric acid is distilled; and when chlorate of potassa is acted upon by oil of vitriol at a gentle heat, peroxide of chlorine being simultaneously produced, as has been already shown. It is also formed when peroxide of chlorine is acted upon by the galvanic current. The most convenient mode of obtaining it, however, is by heating chlorate of potassa until one-third of its oxygen is expelled,



purifying the perchlorate from the chloride by crystallization (the former being far more insoluble than the latter), and distilling the perchlorate with an equal weight of sulphuric acid, first diluted with half its weight of water. The aqueous perchloric acid thus obtained is freed from sulphuric acid by treatment with baryta-water, and from chlorine by digestion with oxide of silver; the dilute acid is concentrated by gentle evaporation.

Properties.—Perchloric acid, when concentrated, fumes slightly on exposure to air; it is colorless, has an oily appearance, and boils at 392°F . (200°C .)

Unlike the other compounds of chlorine with oxygen, this acid does not possess bleaching properties. It is the most stable of the oxides of chlorine, and its affinity for bases is considerable.

The perchlorates are generally formed from the potassa or baryta salts (obtained as above from the chlorates) by mixing their solutions with the silicofluorides or sulphates. They are all soluble, and mostly deliquescent, and are decomposed by heat, like the chlorates, though with less facility. They explode when thrown on ignited charcoal, but are less powerful in their action than the chlorates.

CHLOROPERCHLORIC ACID. $\text{Cl}_3\text{O}_{17} = 2\text{ClO}_7.\text{ClO}_3$.

This acid is formed by the action of light upon chlorous acid. By exposing this gas (perfectly dry) to sunlight or diffused daylight, it is decomposed into perchloric acid, oxygen, and chlorine. If, however, the bottle is immersed in water, and thus submitted to the action of light, at a temperature of 68°F . (20°C .), a reddish liquid is produced, which forms dense fumes when exposed to moist air, and is decomposed by heat. When treated with potassa, it yields 2 equivalents of perchlorate and 1 equivalent of chlorite of potassa; this shows it to have the above-mentioned formula.

Of the above compounds of chlorine with oxygen, five are very similar to each other, namely, ClO , ClO_2 , ClO_3 , Cl_2O_{12} , and Cl_3O_{17} ; it is, therefore, not easy to distinguish them perfectly one from another. Much attention has been paid of late to the oxygen compounds of chlorine by several chemists. Millon adopts a view regarding the constitution of these compounds, by which an easy explanation of the conversion of chloric into perchloric acid, and some other phenomena exhibited by these oxygen compounds of chlorine, is afforded. The following table exhibits the formulæ of these acids, and Millon's view regarding their constitution:—

Hypochlorous acid .	ClO	
Chlorous acid . . .	ClO_2	
Hypochloric acid . .	$\text{ClO}_3 = \text{Cl}_2\text{O}_{12} = 3\text{ClO}_3 + \text{ClO}_7$	
Chloric acid	$\text{ClO}_3 = \text{Cl}_2\text{O}_{12} = \text{ClO}_3 + \text{ClO}_7$	
Chlorochloric acid .	$\text{Cl}_2\text{O}_{12} = 2\text{ClO}_3 + \text{ClO}_7$	
Chloroperchloric acid	$\text{Cl}_3\text{O}_{17} = \text{ClO}_3 + 2\text{ClO}_7$	
Perchloric acid . . .	ClO_7	

CHLORINE AND HYDROGEN.

HYDROCHLORIC ACID, MURIATIC ACID.

HCl. *Eq.* 36.5. *Sp. Gr.* 1.284.

Composition by Volume.—2 volumes of chlorine and 2 volumes of hydrogen combine to form 4 volumes of this acid.

§ 96. Hydrochloric acid has been discovered, in the uncombined state, in a thermal spring in New Grenada (S. America).

Chlorine and hydrogen, when mixed in equal volumes, may be made to combine by exposure to sunlight, to flame, to the electric spark, or to the action of spongy platinum, and of diffused daylight; and also when passed through a red-hot tube. In the four first cases, the combination is attended by explosion.

The affinity of chlorine for hydrogen is so great as to cause the decomposition of most hydrogen compounds. Many organic substances are decomposed by chlorine at ordinary temperatures (oil of turpentine, for example), hydrochloric acid being formed. Others require a high temperature or contact with flame (olefiant or coal-gas, for instance).

Preparation.—The usual method of preparing hydrochloric acid gas is, to heat a mixture of fused chloride of sodium and concentrated sulphuric acid; the gas being dried by passing it through oil of vitriol.

The decomposition is expressed by the equation:—



(The gas being soluble in water, must be collected over mercury, or even by displacement.)

Properties.—Hydrochloric acid is a colorless gas, of a peculiar, suffocating, pungent odor; it does not support respiration or combustion, neither is it combustible. It reddens vegetable blues, but possesses no bleaching properties. It may be liquefied by exposure to a pressure of about 40 atmospheres, at 50° F. (45° 3 C.) It forms a colorless liquid, of lower refractive power than water.

Hydrochloric acid gas forms dense fumes when exposed to damp air, in consequence of its condensing the aqueous vapor; water absorbs it, with a considerable rise of temperature, taking up, at ordinary temperatures, nearly its own weight, or 480 times its volume. If a flask filled with the gas be opened under water, the latter rushes in with great violence.

SOLUTION OF HYDROCHLORIC ACID (formerly called *spirit of salt*) is best prepared by heating a mixture of 6 parts of chloride of sodium and 10 of concentrated sulphuric acid, previously diluted with 4 parts of water, in a capacious glass retort or flask, connected with a set of Woulfe's bottles, arranged similarly to those employed for the preparation of solution of ammonia. The bulk of the water employed for the absorption of the gas increases considerably; the hydrochloric acid obtained in the second bottle is perfectly colorless and pure, having a spec. grav. of about 1.21. The water in the third bottle serves to retain any portion of acid that may escape through the second.

The hydrochloric acid of commerce, *common muriatic acid*, is prepared by heating a mixture of equal equivalents of salt and oil of vitriol in capacious horizontal cast-iron cylinders, and conducting the gas evolved into bottles containing water as above.

This acid generally contains several impurities, the chief of which are sulphuric and sulphurous acids, and chlorine, and at times, also, chloride of arsenic, tin, or

iron (the two former from the commercial oil of vitriol).¹ For modes of testing for impurities in hydrochloric acid, see Analysis, Reagents.

Properties.—Solution of hydrochloric acid, when pure, is colorless, and has a pungent but pure acid odor; when concentrated, it evolves dense fumes on exposure to air; its spec. grav., when in the most concentrated state, is 1.2109; it then contains hydrochloric acid in the proportion of 1 to 6 of water. When boiled, it evolves hydrochloric acid gas, and the boiling-point, which is at first considerably below 212°, rises as the aqueous acid becomes weaker; at a temperature rather higher than 212° F. (100° C.) the acid distils over unchanged; its spec. grav. is then about 1.1.

When metallic oxides are treated with hydrochloric acid, the corresponding chlorides are produced, water being simultaneously formed by the combination of the hydrogen in the acid with the oxygen of the base; the following general formula represents the action of this acid:—



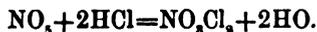
When solution of hydrochloric acid is exposed for some time to the solar rays, chlorine is liberated (Fischer).

Uses of Hydrochloric Acid.—This acid is much used in the manufacture of bleaching-powder, and of glue. It is also employed for dissolving metals, and for preparing the chlorides.

NITRO-HYDROCHLORIC, OR NITRO-MURIATIC ACID. *Aqua regia.*—When 1 part of nitric acid is mixed with 2 or 3 parts of hydrochloric acid, they decompose each other, yielding a yellow fuming liquid of highly corrosive nature, possessing the power of dissolving gold and platinum, which are not acted upon by either of the acids separately.

When a metal is acted upon by this liquid, it is converted into a chloride, an inferior oxide of nitrogen being evolved.

Various opinions have been entertained respecting the true constitution of nitro-muriatic acid. E. Davy believes the liquid to contain a compound of equal volumes of chlorine and nitric oxide, to which he has given the name of *chloronitrous acid* (NO_2Cl_2). Baudrimont obtained from a mixture of 2 parts of nitric acid and 3 of hydrochloric acid, a red gas, condensing at a low temperature, and rapidly absorbed by water; he calls this compound *chloronitric acid*, considers it to have the composition NO_2Cl_2 , and explains its formation by the following equation:—



Gay-Lussac obtained, by submitting the gases evolved by boiling nitro-hydrochloric acid to a freezing mixture, a lemon-yellow liquid, to which he has assigned the formula NO_2Cl_2 , and the name *hypochloronitric acid*, since he views it as hyponitric acid, in which two atoms of chlorine replace two of oxygen.

Its formation would be explained thus:—



By the latter explanation, the evolution of chlorine is accounted for, which is always observed in the preparation of nitro-muriatic acid.

The action appears, however, to be of a more complicated nature, since Gay-Lussac also found the above condensed product to contain a compound of 1 of chlorine to 1 of nitric oxide, NO_2Cl , to which he gave the name of *chloronitrous acid*. According to this chemist, when a metal, such as gold, is acted upon by *aqua regia*, the chlorine evolved from the latter combines with the metal, and chloronitric acid is evolved; hence, he believes the action of nitro-muriatic acid upon gold to be due to the chlorine liberated in the decomposition of the two acids.

¹ The yellow color of the hydrochloric acid of commerce is owing to the presence of sesquioxide of iron, or of free chlorine.

CHLORINE AND NITROGEN.

CHLORIDE OF NITROGEN.

[Eq. according to Davy (NCl₇) 156.] *Sp. Gr.* 1.653.

§ 97. This compound is obtained by passing chlorine gas through a solution of chloride of ammonium, or by inverting a jar of chlorine over a solution of that salt at a temperature of 80.6° F. (32° C.):—



As the gas is slowly absorbed by the solution, an oily liquid is formed on the surface of the latter, falling, after a time, in drops to the bottom of the vessel. These should be carefully collected by means of a syringe, and transferred to a perfectly clean thick cup of lead. The greatest care is necessary in the preparation of this liquid, and it is prudent for the operator to protect himself, as far as possible, from injury arising from probable explosion, by means of gloves and an iron mask.

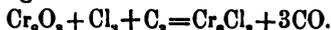
Properties.—Chloride of nitrogen is an oily liquid of a light yellow color, which volatilizes rapidly in air; it does not freeze at —40° F. (—40° C.), and distills below 160° F. (71° C.) Its odor is pungent, and its vapor attacks the eyes. It possesses the remarkable property of exploding when brought into contact with phosphorus, arsenic, fats, essential and fatty oils, &c., or even spontaneously, at times. It is more gradually decomposed by some acids, alkalies, and saline solutions. In the former cases, the products of decomposition are chlorine and nitrogen gases; in cases of more gradual decomposition, the resulting products vary. Manipulations with this liquid have been frequently attended with disastrous consequences. Dulong, the discoverer, lost an eye and several fingers; Davy was also deprived of the sight of an eye through experimenting with it. The quantity operated upon in any case should therefore be very small, the vessels employed must be perfectly clean, and the operator should be properly protected, as recommended above.

Several views may be taken of the composition of chloride of nitrogen. It is not even certain that it contains no hydrogen; its peculiar nature renders it exceedingly difficult to establish its formula with any degree of certainty.

CHLORIDES OF THE METALS.

Chlorine combines with the metals in various proportions, the chlorides of a metal usually corresponding to its oxides. These compounds are either produced by direct combination of chlorine with the metals, or by solution of the oxides in hydrochloric acid, as above stated.

Chlorine also decomposes many metallic oxides forming the corresponding chlorides, oxygen being evolved, or a chlorate, or hypochlorite, simultaneously formed. Some metals, such as zinc and iron, exert a decomposing action on hydrochloric acid, chlorides being formed, and hydrogen liberated. Some chlorides are also produced when chlorine is allowed to act upon the oxides in the presence of a reducing agent (charcoal). Thus, though chlorine will not act on sesquioxide of chromium alone, a mixture of this oxide with charcoal, exposed to the action of chlorine at a high temperature, furnishes sesquichloride of chromium, the oxygen forming carbonic oxide with the charcoal:—



Some chlorides of the metals are liquid at ordinary temperatures (for example,

the bichloride of tin, and the pentachloride of antimony); others are solid. Many metallic chlorides are volatile. They are all soluble in water with the exception of chloride of silver, subchloride of mercury, subchloride of copper, and the protochlorides of gold and platinum. Many of the soluble salts crystallize, from their aqueous solutions, either as anhydrous or hydrated chlorides (*e. g.* chloride of barium, $\text{BaCl} + 2\text{H}_2\text{O}$, and chloride of calcium, $\text{CaCl} + 6\text{H}_2\text{O}$), most of which part with their water of crystallization when heated, while one or two yield hydrochloric acid, metallic oxides remaining behind. Some chlorides in the anhydrous state have a very powerful affinity for water, deliquescing rapidly when exposed to damp air. These are frequently used as desiccators or dehydrators (*e. g.* the chlorides of zinc and calcium).

Oxychlorides form a peculiar class of salts, produced by the combination of the metallic chlorides with oxides of the same metals (for example, oxychloride of lead, $\text{PbCl}_2 \cdot 3\text{PbO}$, and oxychloride of antimony, $\text{SbCl}_3 \cdot 5\text{SbO}_3$).

BROMINE.¹

Sym. Br. Eq. 80. Sp. Gr. 2.966.

§ 98. Bromine was discovered by Balard, in 1826. It is found in minute quantities in sea-water (as bromide of magnesium, or of an alkaline metal); it occurs in rather large quantities in many mineral springs (for instance, those of Kreutznach and Cheltenham), and exists also in many marine plants and animals. Minute quantities of bromine have also been detected in coal.

Preparation.—The solution of alkaline bromides, obtained from evaporated sea or spring-waters, or from the ashes of marine plants, is submitted to a current of chlorine until the yellow color produced no longer increases in depth. The bromine is thus liberated (being replaced in its combinations by chlorine); the liquid is then shaken with ether, by which the bromine is extracted.

The ethereal solution of bromine which rises to the surface, is separated from the saline solution, and agitated with a strong solution of potassa, by which the bromine is converted into bromate of potassa, and bromide of potassium:—



The alkaline solution is then separated from the ether, and evaporated to dryness, the residue fused (whereby the bromate of potassa is converted into bromide of potassium), and afterwards distilled with binoxide of manganese and sulphuric acid, diluted with half its weight of water:—



The bromine thus obtained is freed from water by rectification over fused chloride of calcium. Commercial bromine generally contains bromide of carbon.

Properties.—Bromine is a heavy, mobile liquid, appearing dark brownish-red by reflected light, and hyacinth-red by transmitted light. It solidifies at about $-7^\circ.2 \text{ F.}$ (-22° C.) to a yellowish-brown, brittle, crystalline mass, volatilizes very rapidly when exposed to the air, and boils at about 145° F. (63° C.) Its vapor (*sp. gr.* 5.3933) resembles peroxide of nitrogen in color, and has a very disagreeable pungent smell. It is poisonous (though not quite so powerful in its action as chlorine), giving rise when inhaled to cough, and increased secretion of the mucous membrane, accompanied at times with giddiness and other unpleasant effects. A drop placed on the hand immediately destroys the cuticle, producing a sore. Bromine has a close analogy to chlorine in its chemical relations, the

¹ From *βρῶμος*, a stench.

latter being, however, the more powerful in its affinities. Bromine, nevertheless, combines with great energy with most other elements. Thus, phosphorus and antimony take fire spontaneously, when introduced into bromine vapor. Like chlorine, also, it bleaches organic coloring matters, and for a similar reason.

One part of bromine is soluble in 33.3 parts of water at 59° F. (15° C.) The solution has a yellowish-red color, and gradually decomposes when kept, especially on exposure to light, hydrobromic acid being formed.¹ Bromine gives a yellowish-red color with starch.

Its principal compound with oxygen is bromic acid, BrO₃; with hydrogen it forms hydrobromic acid, HBr. Bromine is also known in combination with carbon, chlorine, and iodine, and forms bromides with many metals, quite analogous to the corresponding chlorides.

BROMINE AND OXYGEN.

§ 99. When bromine is added to a cold dilute solution of fixed alkali, either in the caustic state, or as carbonate, a solution is obtained possessing bleaching properties; the analogy which bromine exhibits to chlorine in so many instances, renders it probable that in this case a compound of bromine and oxygen similar to hypochlorous acid, namely, hypobromous acid, BrO, is formed, producing bleaching compounds when united to bases. Comparatively little is known, however, with regard to the true nature of the above reaction.

BROMIC ACID, BrO₃. Eq. 120.

This acid is produced when bromine-water is mixed with an excess of solution of potassa (*see* Preparation of Bromine), or heated with hypochlorous acid, chlorine being disengaged; it is also formed when pentachloride of bromine is acted upon by potassa:—



Preparation.—Bromic acid is best obtained by decomposing a solution of bromate of baryta with an equivalent quantity of sulphuric acid, separating the sulphate of baryta formed, and concentrating the clear liquid by gentle evaporation.

Properties.—Bromic acid has not been obtained in an anhydrous state. In combination with water it forms a colorless liquid, reddening litmus, and bleaching it after a little time.

It volatilizes when heated, being partially decomposed into bromine and oxygen. In most of its properties it is analogous to chloric acid.

Bromates are mostly soluble in water. When heated to redness, they are decomposed, bromides being in some cases formed, and oxygen evolved; in other cases the oxides are obtained with simultaneous evolution of oxygen and bromine-vapor. They possess explosive properties similar to those of the chlorates.

BROMINE AND HYDROGEN.

HYDROBROMIC ACID.

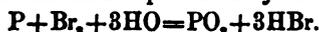
HBr. Eq. 81. Sp. Gr. 2.73.

Composition by Volume.—2 volumes of hydrogen and 2 volumes of bromine form 4 volumes of the gaseous acid.

¹ When a solution of bromine is cooled to nearly the freezing-point of water, crystalline scales are formed, having the formula Br + 10HO.

Bromine and hydrogen may be made to combine directly, by passing them through a heated tube, especially if it contain platinum-sponge. Hydrobromic acid is gradually produced by exposure of bromine, together with water, to the sun's rays; but is most readily formed when those two bodies are brought in contact with some substance having a powerful affinity for oxygen (some de-oxidising agent) such as phosphorous, sulphurous, and arsenious acids, metals, &c. It is also produced with ease by bringing bromine in contact with most hydrogen compounds, such as hydrosulphuric acid, phosphide of hydrogen, hydriodic acid, or ammonia. Alcohol, ether, and many organic substances, likewise convert bromine into hydrobromic acid.

Preparation.—This acid is obtained by gently heating, in a small retort, phosphorus and bromine, together with a very little water, and collecting the gas over mercury. Its formation is represented by the following equation:—



It may also be prepared by moistening 6 parts of crystallized sulphite of soda with 1 part of water, adding 3 parts of bromine, and applying heat.

An aqueous solution of hydrobromic acid is best obtained by passing hydrosulphuric acid gas through water containing a little bromine, and adding fresh quantities of the latter as it disappears by the action of the gas:—



Some sub-bromide of sulphur is formed in the process, which is decomposed by water into hydrobromic acid and sulphurous acid:—



The solution of hydrobromic acid thus obtained is heated rather below ebullition, until the excess of hydrosulphuric acid is expelled, and afterwards separated by filtration from the sulphur.

Properties.—Hydrobromic acid is a colorless transparent gas, of a pungent odor and acid taste. It reddens litmus powerfully, and fumes on exposure to damp air. It liquefies at -92° F. ($-68^\circ.8$ C.), and solidifies at -100° F. ($-73^\circ.1$ C.) It is rapidly absorbed by water, with evolution of heat; the strongest solution of hydrobromic acid has a spec. grav. of 1.29, and fumes on exposure to air; it boils at a temperature below 212° F., being rendered weaker; more dilute acid boils at a higher temperature, and becomes stronger by boiling. When chlorine is mixed with hydrobromic acid, hydrochloric acid is formed, and bromine liberated, chloride of bromine being formed if the chlorine is in excess. Some metals, when brought into contact with hydrobromic acid, decompose it, forming metallic bromides with evolution of hydrogen; the oxides of metals also decompose hydrobromic acid, yielding bromides and water. The properties of metallic bromides will be presently described.

BROMINE AND CHLORINE.—When chlorine is passed through bromine, and the vapors evolved condensed by a freezing mixture, a very volatile reddish-yellow liquid, the chloride of bromine, is obtained. It emits yellow fumes, of a very pungent odor, exciting a flow of tears. If water is present in the bromine, bright yellow crystals of chloride of bromine are obtained.

METALLIC BROMIDES.—These are formed either, as just now stated, by the action of hydrobromic acid on some metals, or on metallic oxides, or by the direct combination of bromine with the metals.

They are solid at ordinary temperatures, fuse when moderately heated, and are volatile at high temperatures. In most of their properties they are very analogous to chlorides; they are decomposed by the action of chlorine, the latter replacing the bromine in its combination with a metal; they are also decomposed by hydrochloric acid, the products being hydrobromic acid and metallic chlorides. Most bromides are soluble in water. They sometimes combine with their corresponding oxides, forming oxybromides, analogous to oxychlorides.

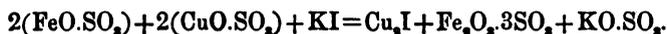
IODINE.¹

Sym. I. Eq. 127.1. Sp. Gr. 4.948.

§ 100. Iodine was first discovered by Courtois, in 1812, and was subsequently submitted to examination by Gay-Lussac (in 1813-14).

Iodine is found in many saline springs and mineral waters (existing in them as iodides of sodium, calcium, or magnesium). It also occurs in very minute quantities in sea-water, but more abundantly in marine plants and animals (sponge). Iodine likewise exists in a few minerals. Small quantities of iodine have recently been obtained from coal.

Preparation.—Various methods are employed for obtaining iodine from the ashes of marine plants, &c. That most generally in use is to evaporate the aqueous extract until most of the other salts have crystallized out, and then to precipitate the mother-liquor with a mixture of two and a half parts of sulphate of iron, and one part of sulphate of copper. The subiodide of copper is thus obtained, the reaction being represented by the following equation:—



Precipitate

The subiodide of copper, when heated with binoxide of manganese and sulphuric acid, yields iodine, which is disengaged in violet vapors, condensing to black crystals as they cool.

A method of preparing iodine from the mother-waters has lately been proposed, in which the iodine is liberated by a mixture of sulphuric and nitric acids, and separated by filtering through lampblack, which takes up the iodine, and yields it again to potassa. The alkaline solution is then evaporated to dryness, the residue ignited, and afterwards distilled with binoxide of manganese and sulphuric acid.

Properties.—Iodine is a grayish-black substance, possessing metallic lustre, and somewhat resembling plumbago in appearance. Its crystalline forms belong to the right prismatic system (the primary form being the acute rhombic octohedron). It is soft and brittle, fuses at 224°.6 F. (107° C.) solidifying to a laminated mass on cooling. It boils at 347° F. (175° C.) passing over into violet vapors,² which condense upon cooling into crystals. Iodine resembles chlorine somewhat in its odor; it may be said to have a marine smell; its taste is very acrid and astringent. Water dissolves iodine very sparingly (one part being soluble in 7000 of water); the solution has a brown color. It is far more soluble in alcohol and ether, forming deep brown-red solutions; and is also soluble to a considerable extent in solutions of hydriodic acid and iodide of potassium. Iodine is destitute of bleaching properties.

Free iodine yields a deep blue color with starch, and imparts a transient yellow stain to the skin, and other organic matters.

This element combines with hydrogen, oxygen, phosphorus, and the metals, like chlorine and bromine; it also unites with the two latter substances.

Iodine is poisonous when taken internally; small quantities may, however, be administered medicinally.

The chief Uses of Iodine depend upon its medicinal properties. It is employed principally to reduce glandular swellings, and in scrofulous diseases. This application of iodine arose from its discovery in the ashes of sponge, for a long period used as a medicinal agent.

¹ From *iodos*, violet-colored.

² The vapor-density of iodine is 8.716.

Iodine is also employed in various forms (sometimes in conjunction with bromine), for photographic purposes. The iodine of commerce is sometimes adulterated with plumbago or sulphide of antimony, &c., which will be left behind when the iodine is volatilized by a gentle heat.¹

IODINE AND OXYGEN.

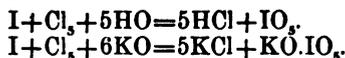
Iodic acid IO₃.
 Periodic acid IO₅.

§ 101. The existence of two other compounds of iodine and oxygen has been asserted by several chemists, although nothing definite has been arrived at with regard to their real nature—namely, iodic oxide, and iodous or hypo-iodous acid.

Salts have been obtained, the composition of which is expressed by the formula, MO.IO; the acid they contain, however, has never been satisfactorily isolated; the ease with which these salts decompose into iodates and iodides, renders it even possible that they are mixtures of those salts.

IODIC ACID, IO₃. Eq. 167.1.

When iodine is left in contact with excess of chlorine, together with a quantity of water, hydrochloric and iodic acids are formed; or, in the presence of potassa, the chloride of potassium and iodate of potassa:—



When iodine is dissolved in an aqueous solution of potassa, iodate of potassa is formed, together with iodide of potassium:—



Preparation.—The best method of obtaining iodic acid, consists in boiling iodine with the strongest nitric acid, in a capacious and long-necked flask, until it is perfectly oxidized, and then expelling the excess of nitric acid by evaporation of the liquid to dryness, resolution in water, and repeated evaporation. It may also be prepared from the iodate of baryta, by boiling nine parts of this salt with two parts of diluted sulphuric acid, filtering off the precipitated sulphate of baryta, and evaporating the clear solution.

Properties.—Iodic acid crystallizes from its solution (previously concentrated to the consistency of syrup) in six-sided tables. These crystals are white and translucent; they are very soluble in water, and but slightly so in alcohol. They contain one atom of water, which is expelled at 338° F. (170° C.); the anhydrous acid thus obtained again yields the hydrate when in contact with water.

Iodic acid, when heated to fusion, is decomposed into oxygen and iodine vapor. It parts with its oxygen when heated with combustible substances; the decomposition is not accompanied with detonation. It is also decomposed by hydrobromic, hydrochloric, hydrosulphuric, and sulphurous acids, the iodine being liberated. This reaction is taken advantage of in testing for sulphurous acid, with a mixture of iodic acid and starch.

Metallic oxides combine with iodic acid in three different proportions, some iodates containing one, some two, and others three atoms of acid to one of base. Iodates are but slightly or not at all soluble in water; they detonate and deflagrate when heated with combustible substances, like chlorates, though not so powerfully. They are converted by heat into metallic iodides, oxygen being

¹ Iodide of cyanogen has also been found in iodine of commerce.

alone liberated; or some evolve oxygen and iodine, the metallic oxides being obtained.

PERIODIC ACID, IO_7 . *Eq.* 188.1.

Preparation.—This acid is formed by passing chlorine through a warm mixture of iodate of soda and caustic soda; periodate of soda is obtained, being deposited as a powder upon concentration of the liquid. The free acid is prepared by precipitating a solution of the periodate in cold dilute nitric acid, with nitrate of lead, boiling the precipitate (periodate of lead) with dilute sulphuric acid, filtering off the sulphate of lead, and evaporating the clear solution, from which the acid is then deposited in hydrated crystals, which lose their water at 320°F. (160°C.).

Properties.—Periodic acid crystallizes in transparent colorless prisms, having the composition $\text{IO}_7 \cdot 5\text{HO}$. They deliquesce in air, fuse at 266°F. (130°C.), and, at about 400°F. ($204^\circ \cdot 5 \text{C.}$) are converted into anhydrous iodic acid. Periodic acid is but slightly soluble in alcohol, and less so in ether. It yields with nitrate of silver a precipitate insoluble in nitric acid. The acid is decomposed by sulphurous acid, hydrochloric acid, and sulphuretted hydrogen, iodine being liberated.

The *periodates* generally are sparingly soluble. In these salts, the five equivalents of water of the hydrated acid are replaced, in part, by base. There are two soda-salts, having respectively the composition, $2\text{NaO} \cdot \text{IO}_7 \cdot 3\text{HO}$ and $\text{NaO} \cdot \text{IO}_7 \cdot 4\text{HO}$. The potassa-salt has the formula $\text{KO} \cdot \text{IO}_7$. The baryta-salt, $2\text{BaO} \cdot \text{IO}_7 \cdot 3\text{HO}$. The lead-salt $3\text{PbO} \cdot 2\text{HO} \cdot \text{IO}_7$. They are decomposed by heat.

IODINE AND HYDROGEN.

HYDRIODOUS ACID, HI_2 .—This acid is said to be formed by exposing a solution of hydriodic acid to the air, or by its contact with excess of iodine.

It has not been obtained in the anhydrous state; its solution is dark-brown, and smells of iodine, which it gradually deposits in crystals on protracted exposure to air.

HYDRIODIC ACID, HI . *Eq.* 128.1. *Sp. Gr.* 4.43.

Composition by Volume.—2 volumes of iodine and 2 volumes of hydrogen produce 4 volumes of hydriodic acid.

This acid is produced when a mixture of iodine-vapor and hydrogen is passed through a redhot tube. It is formed in far larger quantity when hydrogen is passed, together with iodine-vapor, through a tube containing spongy platinum gently heated. In the presence of some substance having a strong affinity for oxygen (*e. g.* phosphorus), iodine decomposes water with formation of hydriodic acid.

Iodine also abstracts the hydrogen from phosphide of hydrogen, hydrosulphuric acid, ammonia, and some organic compounds.

Preparation.—To obtain the gaseous acid, one part of phosphorus, and sixteen parts of iodine, are carefully placed in alternate layers with coarsely powdered glass, and the whole covered with a layer of the glass powder (*Fig. 64*); the mixture is heated very cautiously, a little water afterwards added to decompose the iodide of phosphorus, and the gas collected over mercury, or better, by displacement; a safer method is to dissolve fourteen parts of iodide of potassium in a small quantity of water, to add one part of phosphorus and twenty of iodine, and heat gently; a third method consists in heating three parts of iodine with six of sulphite of soda and one of water. Liquid hydriodic acid is obtained by

introducing together, in a sealed bent tube, one part of iodine and two of persulphide of hydrogen, a small quantity of water being present in the tube at the bend. Upon bringing the mixture (which forms a yellowish-brown liquid), in contact with water, sulphur is immediately separated, and hydriodic acid produced, the greater part of which condenses, in the opposite extremity of the tube, to a yellow liquid. By exposure to a temperature of $-59^{\circ}.8$ F. (-51° C.) it solidifies to a transparent colorless mass.

Properties.—The gaseous acid is colorless and transparent, possessing an acid taste and suffocating odor, similar to that of hydrochloric acid; it fumes on exposure to air, is incombustible, and does not support combustion. Hydriodic acid is absorbed by water to about the same extent as hydrochloric acid.

An aqueous solution is best obtained by passing hydrosulphuric acid gas through water, in which finely-divided iodine is suspended, until the brown color of the liquid disappears; the latter is then separated from the precipitated sulphur by filtration, and maintained at a temperature of somewhat above ebullition until the excess of hydrosulphuric acid is expelled. The production of hydriodic acid is shown by the following equation:—



It is advisable to add the iodine gradually in small quantities, as the solution becomes colorless, agitating the latter repeatedly.

A solution of hydriodic acid may also be obtained by decomposing a solution of iodide of barium by an equivalent proportion of sulphuric acid, and filtering the liquid.

The most concentrated solution boils between 257° and 262° F. (125° and 128° C.) It fumes on exposure to air, and gradually decomposes if kept, oxygen being absorbed and iodine separated. It dissolves a considerable quantity of iodine, forming a brown-red solution.

Hydriodic acid is decomposed when passed with oxygen through a redhot tube, the products being iodine and water. It is also decomposed by chlorine and bromine, with the formation of hydrochloric or hydrobromic acid; by several metals (metallic iodides resulting); and by some few acids (nitric, conc. sulphuric, hypochlorous, &c.).

Metallic oxides, when acted upon by hydriodic acid, are converted into iodides with formation of water.

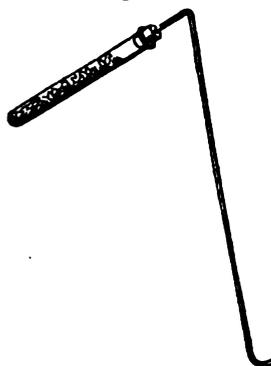
IODIDE OF NITROGEN.—When powdered iodine, or chloride of iodine, is treated with solution of ammonia, a black powder is formed, to which the name of iodide of nitrogen is given.

Its composition is not accurately known; it is probably either NI or NI₂. It possesses highly explosive properties; even when allowed to dry by exposure to air at ordinary temperatures, it frequently explodes spontaneously, being resolved into its elements.

When any quantity is prepared, therefore, it should be divided into several portions while moist, so as to diminish the danger, or risk of total loss, by spontaneous explosion. Friction, a slight blow, or slight elevation of temperature, causes instantaneous explosion.

Iodide of nitrogen decomposes under water, nitrogen gas being evolved, and

Fig. 64.



iodate of ammonia or iodide of ammonium formed, iodine being likewise separated.¹

IODINE AND CHLORINE.—These elements combine to form two compounds:—

1. *The Chloride of Iodine*, ICl , is produced by passing dry chlorine over dry iodine until a perfectly liquid substance is formed, or by distilling one part of iodide of potassium with four parts of chlorate of potassa. This compound is also produced when iodine is dissolved in *aqua regia*. It is a reddish oily liquid, of a pungent odor, attacking the eyes powerfully, and staining the skin. It is very soluble in water, and is also soluble in alcohol; it decolorizes indigo and litmus solutions. It is decomposed by heat into terchloride of iodine, and free iodine. Ammonia decomposes it into chloride of ammonium and iodide of nitrogen.

2. *Terchloride of Iodine*, ICl_3 .—This compound is obtained by treating iodine with an excess of chlorine, or iodic acid with hydrochloric acid. It is an orange-yellow solid, crystallizing in long needles; it melts at between 68° and 77° F. (20° and 25° C.), and evolves chlorine, which it again absorbs as it cools. It is decomposed by water, in which it is not so soluble as the chloride.

IODINE AND BROMINE.—Two compounds are also formed by iodine and bromine; the one by bringing iodine in contact with a small amount of bromine; this is termed the *sub-bromide of iodine*; it is a solid, passing over into reddish-brown vapor when heated. The other compound, the *penta-bromide of iodine*, is produced by the action of excess of bromine upon iodine. It is a dark-brown liquid, pretty soluble in water. Both these compounds yield, on treatment with alkalies, a bromide and an iodate.

METALLIC IODIDES.—These are produced either by the action of iodine on metals, or of hydriodic acid on some metals or metallic oxides. Some are exceedingly soluble in water (alkaline iodides) crystallizing like the chlorides; most iodides are somewhat soluble in water, and a few are decomposed by it into the metallic oxides (which are precipitated), and into hydriodic acid. Many metallic iodides possess beautiful colors. When heated with access of air, the greater number are decomposed, iodine being evolved, and the metallic oxides formed; their solutions are decomposed by chlorine or bromine (or solutions of these elements); they are likewise decomposed by nitric and sulphuric acids. Some iodides also combine with the corresponding oxides, forming oxyiodides.

Chlorine, bromine, and iodine sometimes exert a remarkable and interesting action upon organic substances, consisting in the removal of one or more equivalents of hydrogen, and its replacement by an equivalent quantity of one, or even two, of the salt-radicals, thus giving rise to a very important class of substitution-products.

We may take this opportunity of directing attention to the interesting speculations of Dumas with regard to the remarkable relation observed between the atomic weights of certain elements.

This eminent chemist has pointed out the circumstance that there are certain groups or *triads* of elements, resembling each other in their most important properties, the equivalents of which are in such a ratio that the sum of the extremes is equal to twice the mean. Thus, if the sum of the atomic weights of chlorine and iodine ($35.5 + 127.1 = 162.6$) be divided by 2, the quotient is nearly the atomic weight of bromine (80). Again, half the sum of the equivalents of barium (68.5) and calcium (20) is nearly the equivalent of strontium (43.8). Another triad comprehends potassium, sodium, and lithium. These highly

¹ Bunsen has recently investigated this subject. He found that the compound obtained by the action of ammonia upon an alcoholic solution of iodine had the formula $\text{NI}_3 \cdot \text{NH}_3$, while that precipitated by ammonia from a dilute solution of iodine in *aqua regia* was $4\text{NI}_3 \cdot \text{NH}_3$.

interesting facts, taken in conjunction with the circumstance that the members of the same triad are often found in association, appear to render it not altogether improbable that the compound nature of the middle term, at least, of each triad may hereafter be demonstrated.

FLUORINE.¹

Sym. F. Eq. 19.

§ 102. The process of etching on glass by means of fluor-spar was known as far back as 1670. Scheele, in 1771, declared fluor-spar to be a compound of lime with a peculiar acid, which was regarded by him and several other chemists who subsequently investigated the subject, to be an oxygen compound of an unknown element. In 1810, Ampère first considered the acid to be a compound of hydrogen and fluorine.

Fluorine is found, though not very abundantly, in the mineral kingdom, in combination with various metals (as in apatite, fluor-spar, topaz, &c.); it also occurs in minute quantities in human urine, in bones, teeth, and also in the ashes of some plants, and in sea-water. It is also said to exist in small quantity in blood and milk.

Nothing can be said with regard to the nature of fluorine itself, since repeated attempts made by various eminent chemists to isolate it have not been attended with any satisfactory result. Its powerful affinities, which appear to surpass even those of oxygen, cause it to unite with other substances at the instant of its liberation; its properties in the uncombined state are hence quite unknown; it appears probable, however, from the nature of its compounds, that it is a gaseous element, much resembling chlorine.

Those investigators who have believed that they obtained it in the separate state, describe it, for the most part, as a gas similar to chlorine.

Fluorine combines with most of the metals, and also with hydrogen, boron, silicon, sulphur, selenium, and phosphorus; its compounds are analogous in their properties to those of chlorine, bromine, and iodine, with which elements, as with oxygen, it evinces no tendency to unite.

FLUORINE AND HYDROGEN.

HYDROFLUORIC ACID.

HF. Eq. 20. Sp. Gr. 1.0609.

Preparation.—This acid is obtained by heating together one part of finely powdered fluor-spar (free from any silica) and two parts of oil of vitriol, in a leaden retort, in which no solderings must be used. The product is collected in a receiver of lead, loosely adapted to the neck of the retort, and surrounded by a freezing mixture. The formation of hydrofluoric acid is explained by the following equation:—



The acid must be preserved in bottles of lead or gutta percha (vessels of gold or platinum might also be employed for its preparation and preservation).

Properties.—Hydrofluoric acid is a colorless, very volatile liquid, boiling not

¹ From *fluo*, to flow, on account of its solvent properties.

much above 59° F. (15 C.)¹ It fumes when in contact with air, has a pungent odor, powerfully attacks the respiratory organs, and is highly corrosive; if dropped upon the skin it immediately produces a very painful sore, even its vapor produces pains under the nails. Hydrofluoric acid decomposes all compounds of silicon on account of the powerful affinity of fluorine for that element; hence it immediately corrodes glass and porcelain, and cannot, therefore, be prepared or preserved in vessels of those materials.

Hydrofluoric acid is decomposed by the galvanic current; many metals also decompose it, fluorides being produced, and hydrogen disengaged.

Most metallic oxides decompose it, forming fluorides and water. A solution of hydrofluoric acid is best obtained by placing in the leaden or platinum receiver of the apparatus described above, a quantity of water just sufficient to cover the mouth of the retort neck.

The hydrated acid is a thin colorless liquid, fuming when concentrated.² It is in the state of aqueous solution that hydrofluoric acid is found in commerce. It must be preserved in vessels of lead or of gutta-percha.

Metallic fluorides may be obtained as above stated, by the action of some metals, and of metallic oxides, upon hydrofluoric acid; volatile metallic fluorides may be formed by heating a mixture of fluor-spar, the metallic oxide, and oil of vitriol. The fluorides of the metals resemble the metallic chlorides in most respects. Many of them are soluble in water, the solutions act upon glass. Some of them, when heated in a flame containing aqueous vapor, are decomposed into metallic oxides and hydrofluoric acid. They are also decomposed by chlorine in presence of water, and by several powerful acids, such as sulphuric and nitric acids, the sulphates or nitrates being produced, and hydrofluoric acid disengaged.

Several metallic fluorides combine with an equivalent of hydrofluoric acid, forming compounds soluble in water and reddening litmus. Their composition is expressed by the formula MF.HF.

Hydrofluoric acid is extensively employed for etching glass.

SULPHUR.

Sym. S. Eq. 16. Sp. Gr. 2.087.

§ 103. Sulphur occurs in an uncombined state in volcanic districts, and also in masses of sulphate of strontia. It is found in combination with bases as sulphuric acid, occurs combined directly with metals (as sulphides), and exists also in many organic substances.

Preparation.—In Sicily, the volcanic sulphur is separated by distillation from earthy matters. Sulphur is also prepared in England and Germany by roasting or distilling iron-pyrites (bisulphide of iron).

Sulphur exists in commerce in three forms, to which the names of *roll sulphur*, *flowers of sulphur*, and *milk of sulphur*, have been given.

The flowers of sulphur are obtained by conducting the vapor of sulphur into capacious chambers, the sides of which are kept cool; the sulphur condenses in the form of a fine crystalline pale yellow powder. When the sides of the cham-

¹ The liquid acid is stated by Louyet to be a hydrate. He found that, when passed over anhydrous phosphoric acid, the latter deliquesced, and no liquid was condensed in the cooled receiver. This chemist arrived at the conclusion that hydrofluoric acid is a gas at -12° C. (10°.5 F.), under ordinary pressure, and does not exert a sensible action upon glass.

² The specific gravity of the strongest liquid acid (1.06) is increased to 1.25 by the addition of a certain amount of water.

ber become hot, the sulphur fuses, and, trickling down, collects at the bottom, and is run into cylindrical moulds; in this state it is called roll-sulphur.

Milk of sulphur is prepared by adding a slight excess of acid to a solution of sulphur prepared by boiling flowers of sulphur with milk of lime or potassa; the sulphur is precipitated as a fine, nearly white powder, which is collected, washed, and dried. It appears yellowish-gray when dry, and is considered by some chemists to be a compound of sulphur and water. (For the preparation of milk of sulphur see § 161).

Properties.—Sulphur is a pale yellow solid, devoid of taste or smell. It is dimorphous; when native, or crystallized from its solution in bisulphide of carbon, or chloride of sulphur, its form is that of the acute rhombic octohedron; when crystallized by fusion, it is obtained in long thin rhombic prisms.

The two varieties of crystals of sulphur appear to be mutually convertible, their form depending upon the temperature to which they are exposed; thus, if a rhombic octohedron of sulphur be gently warmed in the hand, it becomes opaque, and finally splits, which is apparently due to its change into an aggregation of crystals belonging to the oblique prismatic system.

In the amorphous state, sulphur is opaque. When heated, it exhibits a singular instance of *allotropy*.¹ It melts at 226° F. (107°.8 C.) to a brownish-yellow, transparent, thin, oily fluid; at about 320° F. (160° C.) it begins to become red and viscid; as the temperature rises, it gradually becomes so thick that it will scarcely run out of an inverted vessel. Beyond a certain temperature (about 482° F., 250° C.) it again becomes more fluid, though not so much so as at 240° to 248° F. (116° to 120° C.), and retains a brownish-red color. If it is then allowed to cool gradually, it first returns to the viscid state, then, on cooling still further, once more becomes quite liquid. When cooled rapidly, it does not pass through the intermediate viscid state. If allowed to drop into water when it is in its most fluid state, it solidifies directly to a brittle mass of the ordinary light-yellow color; but if immersed in water when near its boiling point, it is converted into a soft reddish-brown transparent mass, capable of being kneaded or drawn out into threads with the fingers; sulphur in this state is frequently used for taking impressions, as it again becomes (after the lapse of a few days) hard, yellow, and crystalline.

Sulphur boils at about 800° F. (315° C.), being converted into an orange-colored vapor, which possesses a peculiar though not powerful odor, and condenses to small drops upon a cool surface. The density of sulphur-vapor is 6.617.

When heated in air to above 560° F. (293°.3 C.), sulphur takes fire, burning with a pale blue flame. The resulting vapors are very suffocating, and consist of sulphurous acid, which is the only compound produced to any extent by the direct combination of sulphur and oxygen. In presence of moisture, a trace of sulphuric acid is also formed.

Sulphur is a very bad conductor of heat and electricity, becoming highly electric by friction.

It is insoluble in water, but soluble, though sparingly, in alcohol and ether, more soluble in the oils, in subchloride of sulphur, and bisulphide of carbon.²

¹ The term allotropy is now frequently used to denote a property possessed by several substances, of existing in different states without undergoing any important modification of their chemical nature. No satisfactory explanation can as yet be given of this remarkable property; it appears probable, however, that the bodies in question are induced by certain circumstances to undergo a peculiar alteration in their physical structure (or the arrangement of their atoms), and thus become endowed with properties so different from those they originally possess, that they would at once pass for distinct substances if their identity were not proved by their chemical character.

² It has been observed that sulphur, in some forms, is insoluble in alcohol, ether, and bisulphide of carbon. This is the case with a portion of the sulphur precipitated by the action of water upon the chloride of sulphur, by the action of hydrochloric acid upon

When boiled with strong nitric acid, it is converted into sulphuric acid. It is endowed with powerful affinities. It forms several compounds with oxygen.

With hydrogen it forms pentasulphide of hydrogen (HS_5) and hydrosulphuric acid (HS). It also combines in several proportions with carbon (the principal compound being bisulphide of carbon, CS_2), and forms compounds with chlorine, phosphorus, and boron. It unites with metals, forming sulphides, analogous in most instances in their composition to the oxides.

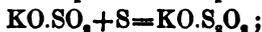
Uses of Sulphur.—This substance is extensively used in the manufacture of gunpowder and of lucifer matches; it is also employed as a source of sulphurous acid for bleaching purposes, and for the preparation of sulphuric acid. Of late years, the application of sulphur in the manufacture of what is called vulcanized Indian-rubber has acquired considerable importance. It is also frequently applied as a remedial agent in cutaneous diseases.

SULPHUR AND OXYGEN.

Hyposulphurous acid . . .	S_2O_5	Tetrathionic acid . . .	S_4O_8
Sulphurous acid . . .	SO_2	Pentathionic acid . . .	S_5O_{10}
Hyposulphuric acid . . .	S_2O_6	Sulphuric acid . . .	SO_3
Trithionic acid . . .	S_3O_6		

HYPOSULPHUROUS ACID, S_2O_5 . *Eq.* 48.

§ 104. This acid is produced in various ways in combination with bases, but cannot be obtained in a separate state. It may be produced by boiling an aqueous solution of an alkaline sulphite with sulphur:—



or by fusing a mixture of sulphur and an alkaline hydrate at a moderate heat, an alkaline pentasulphide is simultaneously produced:—



It is also produced by the exposure of the hydrosulphate of an alkaline sulphite to the air.

Properties.—It has already been stated that hyposulphurous acid cannot be isolated, for, when separated from its salts, it immediately resolves itself into sulphurous acid and sulphur. Its combinations with bases are termed hyposulphites; these last generally consist of one equivalent of acid to one of base. The hyposulphites of the alkalis and alkaline earths are soluble in water. When heated out of contact with air, they are decomposed, water, sulphur, and hydrosulphuric acid being evolved, and a mixture of sulphite and sulphate of the base remaining behind.

The aqueous solution of an alkaline hyposulphite does not alter on exposure to air, unless excess of the alkali be present, in which case it gradually becomes oxidized until a sulphate is formed.

These salts are decomposed by stronger acids, the solution remaining clear at first, but gradually becoming milky (especially when heated) from deposition of sulphur, and evolving sulphurous acid.

Bromide, iodide, and chloride of silver (the latter when freshly precipitated), are soluble in an alkaline hyposulphite. This property has led to the extensive

solutions of hyposulphites, and with that formed when hydrosulphuric acid acts upon sulphurous acid in the presence of water. This modification of sulphur has been found to fuse at a higher temperature than ordinary sulphur, but if maintained between 220° and 248° F. for some time, it is gradually changed, enters into fusion, and is afterwards found to be perfectly soluble in bisulphide of carbon.

use of hyposulphite of soda in photography, for removing from the picture, after its exposure to light, the sensitive coating of iodide of silver.

SULPHUROUS ACID.

SO_2 . Eq. 32. Sp. Gr. 2.234.

Composition by Volume.—1 volume of sulphur-vapor and 6 volumes of oxygen form 6 volumes of sulphurous acid.

Sulphurous acid occurs in volcanic districts, in the gaseous state, and in solution in various springs.

It is produced by the combustion of sulphur in oxygen, by heating sulphur with many metallic oxides, by the deoxidation of sulphuric acid, and by the decomposition of subchloride of sulphur by water.

Preparation.—Concentrated sulphuric acid is heated with copper-clippings, in a flask furnished with a funnel-tube and evolution-tube, and the gas disengaged passed through a small quantity of water, to detain any sulphuric acid that may be carried over. Another method is to heat charcoal in a coarse powder, with sufficient sulphuric acid to wet it thoroughly; a mixture of carbonic and sulphurous acids is thus obtained.

The following equation shows the formation of the gas by the first-named process:—



while the second method is thus represented:—



The latter process can only be applied when the presence of carbonic acid is of no consequence. A good method of obtaining the pure gas is, to heat in a long tube a mixture of one part of sulphur with three of black oxide of copper, covered with a layer of the latter, which is first heated:—



If the gas is required dry, it must be passed through a tube containing fragments of chloride of calcium. Being soluble in water, it must be collected over mercury, or by downward displacement.

Properties.—Sulphurous acid is a colorless gas, incombustible, and a non-supporter of combustion, possessing a suffocating smell and peculiar taste; it is highly injurious in its effects when respired, and generally produces a hard cough, which lasts for some time. Sulphurous acid possesses bleaching properties; this is probably the result of its great affinity for oxygen; it does not, however, permanently destroy vegetable colors, like chlorine, since they are restored by the addition of stronger acids, probably because a colorless compound of sulphurous acid with the coloring matter is formed, which is decomposed by the stronger acid.

This gas may be liquefied by pumping it into a tube previously exhausted and cooled, until the pressure obtained amounts to 4 or 5 atmospheres; or by passing the gas, perfectly dried, as above, into a bottle surrounded with a freezing mixture of equal weights of ice and salt, and provided with an exit-tube. The liquid obtained by these methods must be preserved in sealed tubes. It is transparent and colorless; its sp. gr. is 1.45; it boils at 14° F. (-10° C.)

The cold produced by its reconversion into the gaseous state is very intense; if poured upon water, the latter freezes immediately, even in a redhot crucible.

By exposure of this liquid to the intense cold produced by a mixture of ether and solid carbonic acid, or by allowing it to evaporate very rapidly, it is converted into white flakes.

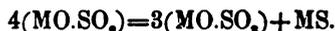
If moist sulphurous acid gas is passed through a redhot tube, it is decomposed into sulphur and sulphuric acid; if the gas is mixed with hydrogen, the products are water and sulphur; if the redhot tube contains charcoal, carbonic oxide and

sulphur are obtained. Some metals, on being heated in sulphurous acid gas, are converted into sulphides and oxides. Sulphurous acid is converted by nitric acid into sulphuric acid; and it acts as a powerful deoxidizer, on account of its great affinity for oxygen.

Water dissolves a considerable quantity of sulphurous acid; the solution has a peculiar acid taste, and the odor of burning sulphur. On exposing it to the air, some of the gas escapes, while a portion is converted into sulphuric acid. By subjecting moist gaseous sulphurous acid to a temperature of about 17°.6 F. (−8° C.), a crystallized hydrate of this acid is obtained, the composition of which appears to be $\text{SO}_2 + 9\text{HO}$. The crystals remain solid until heated to about 39°.2 F. (4° C.), when they fuse, evolving sulphurous acid.

The salts of sulphurous acid, or *sulphites*, are obtained by passing a current of the gas into water containing the bases, or their carbonates, suspended in it. They are inodorous, and have a sharp taste, similar to that of the acid.

The sulphites of the alkalis are soluble in water, as are also all acid sulphites; many others which are insoluble may be dissolved in a solution of sulphurous acid. They are decomposed by stronger acids, with evolution of sulphurous acid. Some sulphites evolve their acid when heated; others are resolved into sulphate and sulphide, thus:—



The sulphites of most heavy metals, when heated with a substance having an affinity for oxygen, such as charcoal, are reduced to sulphides. They undergo gradual oxidation on exposure to air, particularly in the presence of moisture, sulphates being produced.

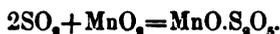
Uses of Sulphurous Acid.—Sulphurous acid and alkaline sulphites are frequently used as reducing or deoxidizing agents; many oxides are at once reduced to the metallic state (gold, silver, mercury, &c.), by its action, while others part with a portion of their oxygen. Sulphurous acid is likewise extensively used for bleaching silken and woollen goods and straw plait, and also for disinfecting clothes.

Bisulphite of lime has been recently applied in the process of refining sugar. The property which sulphurous acid possesses of destroying organic ferments is made use of in order to purify the interior of casks used for wines, &c., in which a little sulphur is generally burnt previously to using them a second time.

HYPOSULPHURIC ACID (*also* DITHIONIC ACID).



When finely powdered binoxide of manganese is diffused through water, and a current of sulphurous acid passed into the latter, an elevation of temperature ensues, and a solution of hyposulphate of manganese, containing a little sulphate, is obtained:—



The temperature of the liquid should be kept low during the operation, since the amount of sulphate of manganese formed appears proportionate to the increase of temperature. The solution obtained is decomposed by baryta-water, which removes the sulphuric acid and protoxide of manganese, the former as sulphate of baryta, and the latter as hydrated oxide. By adding to the filtered solution of hyposulphate of baryta sufficient dilute sulphuric acid to precipitate the baryta, and filtering off the sulphate, a solution of hyposulphuric acid is obtained.

Properties.—Hyposulphuric acid does not exist in the anhydrous state; when the solution is concentrated *in vacuo*, it yields a heavy, transparent, inodorous, and strongly acid liquid.

If heated to 212° F. (100° C.), it is decomposed into sulphurous and sulphuric acids:—



On exposure to air, it is gradually converted into sulphuric acid.

The *hyposulphates* are soluble in water, and crystallize with facility. When heated, they evolve sulphurous acid, and are converted into sulphates:—



They are decomposed by strong acids, and if heat be applied, the sulphates are produced, and sulphurous acid evolved (which is oxidized if nitric acid be employed).

Hyposulphuric acid is said to be formed from sulphurous acid, by imperfect exposure to air for a long period.

SULPHURIC ACID.

SO₃. *Eq.* 40.

§ 105. This acid occurs in large quantities in the vegetable and mineral kingdoms, in combination with various bases (such as the alkalis, alkaline earths, the oxides of iron, copper, lead, zinc, alumina, &c.).¹

Sulphuric acid is produced by the action of 1 volume of oxygen upon 2 volumes of sulphurous acid, in the presence of water, and by the introduction of red-hot platinum into the mixture. It is also formed by the oxidation, in various ways, of the lower oxides of sulphur.

It has recently been shown by Wöhler that sulphuric acid is formed in large quantity, when a dry mixture of 2 volumes of sulphurous acid and 1 volume of oxygen is passed over certain metallic oxides heated to dull redness in a glass tube. The formation of sulphuric acid was observed to take place with very great facility under the influence of a mixture of oxide of copper and sesquioxide of chromium, prepared by precipitation. The same amount of oxide appeared capable of producing an unlimited quantity of sulphuric acid.

ANHYDROUS SULPHURIC ACID.

SO₃.

Preparation.—This compound is obtained by distilling, at a gentle temperature, the most concentrated liquid sulphuric acid, commonly known as fuming, or *Nordhausen sulphuric acid*, in a small retort, to the neck of which is properly fitted a dry receiver, surrounded with ice. The corrosive property of the acid renders impossible the employment of cork or luting in the construction of the apparatus.

The first portion of the acid which passes over is anhydrous, and will condense to a white crystalline solid.

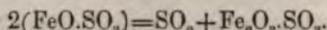
The anhydrous acid may also be obtained by distilling hydrated sulphuric acid with anhydrous phosphoric acid, the affinity of the latter for water being considerably more powerful than that of anhydrous sulphuric acid.

Properties.—This substance crystallizes in groups of long thin needles, which are opaque and white. Its spec. grav. is 1.97. When gently heated, it fuses, yielding a liquid generally possessing a brownish tint, owing, probably, to a trace of organic matter which the acid decomposes. It boils at between 125°.6 and 132°.8 F. (52° and 56° C.); its vapors are colorless in the absence of moisture. Its affinity for water is so powerful that, when brought together with

¹ Sulphuric acid has been discovered, in the uncombined state, in a thermal spring in New Granada (S. America).

the latter, it makes a violent hissing noise, and evolves a considerable amount of heat. The perfectly dry acid is said not to redden litmus-paper; it chars many organic substances at the ordinary temperature. When exposed to moist air, it evolves dense white fumes, and becomes gradually converted into hydrated sulphuric acid, or oil of vitriol.

FUMING, OR NORDHAUSEN SULPHURIC ACID, $2\text{SO}_3 \cdot \text{HO}$, is obtained by the distillation of basic sulphate of sesquioxide of iron, which is prepared by heating crystals of green vitriol ($\text{FeO} \cdot \text{SO}_3 + 7\text{HO}$), when water is at first disengaged, and latterly sulphurous acid, the decomposition being represented by the following equation:—



If this basic sulphate of sesquioxide of iron, which still retains a little water, be exposed to a high temperature, the Nordhausen acid distils over. It is a somewhat viscid liquid, generally of a light-brown color (owing to organic matter), of the spec. grav. 1.896.

When cooled down to a little below 32°F . (0°C .), it solidifies to a crystalline mass. It fumes on exposure to air, owing to its powerful affinity for water; when subjected to distillation, the first portion that passes over consists of anhydrous sulphuric acid, which solidifies in the receiver; the quantity of the latter obtained in this way frequently amounts to 25 per cent. of the fuming acid. The residue in the retort, after this has passed over, is oil of vitriol, or ordinary sulphuric acid. This fuming acid evolves much heat, and frequently hisses, when thrown into water.

CONCENTRATED SULPHURIC ACID—(OIL OF VITRIOL). $\text{HO} \cdot \text{SO}_3$.

This acid, which is generally considered to be the mono or protohydrate of sulphuric acid, is prepared in spacious leaden chambers, the floors of which are covered with water, and into which are simultaneously passed sulphurous acid and nitrous, or nitric acid vapors, atmospheric air, and jets of steam. The sulphurous acid is now generally prepared for this purpose by burning sulphur in a small furnace, built against the wall of the chamber; the nitrous, or nitric acid vapors, are obtained by heating a mixture of nitre and oil of vitriol, which is usually

Fig. 65.



contained in a vessel, *b*, heated by the flame of the burning sulphur. A small boiler, *a*, erected on one side of the chamber furnishes the jets of steam, and valves are provided for the due admission of air. After the water at the bottom of the chamber has attained a certain specific gravity (1.35 to 1.50) from the absorption of sulphuric acid, it is drawn off, and a fresh quantity introduced, which in turn acts upon fresh portions of sulphurous acid, so that a small quantity of nitrous vapor operates as a continuous vehicle for conducting oxygen from the air to the sulphurous acid.

The presence of aqueous vapor is indispensable to the production of sulphuric acid; if sulphurous acid and peroxide of nitrogen gases are mixed when perfectly dry, they have no action upon each other; when a small quantity of moisture is present, however, they form a white crystalline substance, which is immediately decomposed into sulphuric acid and binoxide of nitrogen upon the introduction of more aqueous vapor. This experiment may be conveniently

made in a glass globe on a small scale. If the supply of aqueous vapor be therefore but small in comparison to that of the mixed gases, the sides of the vessel become coated with the above crystalline compound, which disappears upon the introduction of a fresh supply of steam. When the dilute sulphuric acid at the bottom of the chamber has attained a certain specific gravity, it is drawn off, and is concentrated by evaporation in shallow leaden vessels till it attains a spec. grav. of 1.70, when it is transferred into vessels of glass or platinum (still of the latter material being generally used), and boiled down until its spec. grav. is 1.84, when it constitutes the oil of vitriol of commerce.

The theory of the formation of sulphuric acid cannot be said to be thoroughly understood; the following appear to be the most important reactions that take place in the leaden chamber. The peroxide of nitrogen (NO_2), or nitric acid vapors, being made to mix, in the presence of water, with sulphurous acid, convert the latter into sulphuric acid by parting with a portion of their oxygen; the binoxide of nitrogen resulting from this action, absorbing fresh oxygen from the air introduced into the chamber, becomes again converted into hyponitric acid. It would appear that the formation of the crystalline compound is accidental, and must be attributed to a deficient supply of water.

Various other methods have been suggested for the preparation of sulphuric acid, though the above is the only one employed on a large scale. One of these methods consists in passing a mixture of sulphurous acid and moist air through a tube containing platinum-sponge, or balls of very fine platinum wire, or even pumice-stone. Sulphurous acid, when mixed with moist oxygen or air, in contact with finely divided platinum, becomes immediately converted into sulphuric acid.

Commercial oil of vitriol generally contains various impurities, especially if iron or copper pyrites be substituted for sulphur as sources of sulphurous acid. The most common are sulphate of lead, derived from the leaden chamber or evaporating-pan; the oxides of nitrogen, and sometimes also arsenic and selenium, may be detected in it (the latter impurities arising from the sulphur).

The pure monohydrated sulphuric acid is obtained by rectifying oil of vitriol, free from arsenic and oxides of nitrogen,¹ or by distilling Nordhausen or fuming sulphuric acid; the anhydrous acid is first obtained from the latter, and the last portion that distils over is pure oil of vitriol.

PROPERTIES OF THE MONOHYDRATED ACID.—It is an oily colorless liquid, of specific gravity 1.848; it freezes at -29°F. (-34°C.), and boils at 590°F. (310°C.), its vapors being colorless and very suffocating: they form dense fumes on exposure to air. It possesses a powerful affinity for water, evolving much heat when diluted. This is partly owing to the condensation of volume, since a mixture of sulphuric acid and water will be found to occupy much less space than did the two liquids before mixture.

The avidity with which sulphuric acid absorbs water (from air or gases for example) renders this substance a valuable dehydrating or desiccating agent in the hands of the chemist. In consequence of this powerful affinity of sulphuric acid for water, organic substances are charred when immersed in it; the acid assuming a brown tinge, due to the separation of carbon, part of the hydrogen and oxygen having been converted into water, and removed by the sulphuric acid.

When the vapor of sulphuric acid is passed through a porcelain tube at a high red heat, it is decomposed into sulphurous acid and oxygen. Charcoal decom-

¹ The distillation of sulphuric acid must be conducted with great care, on account of the succussions that generally take place when it is boiled, owing to the irregular disengagement of vapor; the precautions mentioned at § 41 should be attended to, since the violence of the succussions is thereby considerably decreased; Berzelius recommends, however, in addition, that the retort be heated at the sides only, and never at the bottom.

poses sulphuric acid when heated with it, the products being sulphurous and carbonic acids. Many metals also decompose sulphuric acid with the aid of heat, sulphurous acid being evolved, and sulphates of the metallic oxides produced.

BIHYDRATED SULPHURIC ACID, 2HO.SO_3 .—Produced by the combination of one equivalent of sulphuric acid and two of water, is a liquid having the specific gravity 1.78; it solidifies to transparent colorless six-sided prisms, at about $39^\circ.2$ F. (4° C.); when it is heated to between 401° and 410° F. (205° and 210° C.), one equivalent of water is expelled together with some sulphuric acid, and oil of vitriol is obtained.

TERHYDRATED SULPHURIC ACID, 3HO.SO_3 .—This hydrate of sulphuric acid has a spec. grav. of 1.632; it boils at between $379^\circ.4$ and $390^\circ.2$ F. (193° and 199° C.), no acid being volatilized at that temperature. When dilute sulphuric acid is evaporated *in vacuo* over oil of vitriol, this hydrate is left.

COMBINATIONS OF SULPHURIC ACID WITH METALLIC OXIDES.—Sulphuric acid may be considered as the most powerful acid, since, under ordinary circumstances, it expels all others from their combinations. There are two classes of sulphates; the neutral salts, represented by the general formula, MO.SO_3 , and the bisulphates, MO.SO_3 , HO.SO_3 , or MO.HO.2SO_3 . Many of the neutral sulphates are soluble with difficulty, or wholly insoluble in water. The acid sulphates of the alkalis, and some other oxides, are far more soluble than the corresponding neutral salts.

Sulphates are decomposed by ignition with charcoal; in some cases the metallic sulphides are obtained, carbonic oxide and carbonic acid being disengaged; in others, the metals are reduced, and carbonic oxide, sulphurous and carbonic acids evolved. Many sulphates are decomposed by a current of hydrogen at a red heat, water, and the metallic sulphides being produced. Alkaline sulphates existing in somewhat dilute aqueous solutions (for example, in mineral waters) undergo gradual decomposition when allowed to remain in contact with organic matter; the sulphur parts with its oxygen, which oxidizes the organic matters, and metallic sulphides, or hydrosulphuric acid, are produced.¹ A particle of cork allowed to fall accidentally into the water, is sufficient to induce this decomposition.

Uses of Sulphuric Acid.—The great facility and cheapness with which sulphuric acid may be manufactured on a large scale, has rendered it by far the most valuable chemical agent in the manufactures and arts. The important functions which it exercises in the manufacture of soda need merely be adverted to.

As a chemical agent, sulphuric acid is also one of the highest importance. In consequence of its powerful affinities for bases, it may be employed to separate most other acids from their combinations; its affinity for water is also turned to advantage by the chemist, as already mentioned. One of the most recent uses to which sulphuric acid has been applied as a reagent, is met with in the process of silver-refining, when auriferous silver is boiled with oil of vitriol, which dissolves the silver in the form of sulphate, without acting upon the gold. (The silver is precipitated from the solution by means of slips of copper.) The Nordhausen sulphuric acid possesses the property of dissolving indigo, yielding a solution much used by dyers.

§ 106. We have written the formula of hydrated sulphuric acid (HO.SO_3), consistently with the older view, which regards it as a compound of water with the anhydrous acid, SO_3 . The circumstance, however, that SO_3 is not capable of entering into combination with bases, and does not appear to possess the properties of an acid, until it has been brought in contact with water, has led many

¹ It has been observed that well-water, containing much sulphate of lime, which had been shaken with an ethereal oil and allowed to stand in a close vessel for some weeks, became charged with hydrosulphuric acid, while the oil diminished in bulk, and carbonate of lime separated from the water.

chemists to believe that the so-called hydrated acid is really the hydrogen-acid of a radical SO_4 ; for



and sulphuric acid then becomes analogous to hydrochloric acid, containing the compound radical SO_4 in place of chlorine.

Upon this hypothesis many of the reactions of sulphuric acid could be explained in a far simpler manner than upon the older view; compare, for example, its action upon zinc:—



The latter equation is quite similar to that which represents the action of hydrochloric acid upon zinc:—



Upon this theory, the sulphates would no longer be regarded as compounds of sulphuric acid with the metallic oxides, but as haloid salts, composed of metals combined with the radical SO_4 . According to the older view of the constitution of sulphuric acid, sulphates are formed by the substitution of an equivalent of base for the equivalent of water in the hydrated acid, whereas the new theory regards them as produced by the replacement of the hydrogen by a metal, the oxygen of the oxide combining with the displaced hydrogen to produce water; the following equations exhibit the formation of sulphate of copper upon both views:—



It will be seen that, in the latter case, the formation of a sulphate is analogous to that of a chloride, by the action of hydrochloric acid upon a metallic oxide:—



This binary theory, as it is generally termed, has been applied to other acids and salts, the formulæ of some of which are given in the subjoined list, in juxtaposition with those which they would have according to the new view:—

	Old view.	New view.
Nitric acid	$HO.NO_3$	HNO_3
Nitrates	$MO.NO_3$	MNO_3
Metaphosphoric acid	$HO.PO_3$	HPO_3
Metaphosphates	$MO.PO_3$	MPO_3
Pyrophosphoric acid	$2HO.PO_3$	H_2PO_7
Pyrophosphates	$2MO.PO_3$	M_2PO_7
Tribasic phosphoric acid	$3HO.PO_3$	H_3PO_8
Tribasic phosphates	$3MO.PO_3$	M_3PO_8

One great objection to this theory is, that the new radicals are hypothetical; neither SO_4 , NO_3 , PO_3 , PO_7 , nor PO_8 , has been obtained in the separate state. This, however, would not form an insuperable bar to its adoption, since the chemist does not refrain, in other cases, from assuming the existence of a radical when the behavior of a series of compounds appears to justify such an assumption.

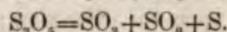
LESS IMPORTANT OXIDES OF SULPHUR.

§ 107. TRITHIONIC ACID, S_3O_8 . Eq. 88.—This acid is prepared by boiling a saturated solution of bisulphite of potassa, for some days, with flowers of sulphur (until the yellow color at first observed disappears), and filtering while hot. Trithionate of potassa crystallizes out, and is separated from excess of sul-

¹ MO representing any basic protoxide.

phur by solution in a small quantity of tepid water. The potassa-salt is afterwards decomposed by means of tartaric or perchloric acid; an aqueous solution of the acid is thus obtained, which may be concentrated by gentle evaporation.

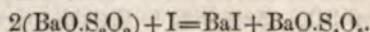
Properties.—The aqueous solution of this acid is colorless, transparent and inodorous; it is not a very powerful acid. It easily decomposes, even at ordinary temperatures, being resolved into sulphur, sulphurous, and sulphuric acid



Heat accelerates the decomposition. It is also decomposed by nitric acid into sulphuric acid and sulphur.

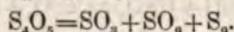
The trithionates have not been much studied; the potassa salt is the only one known. It is easily decomposed by heat, or by more powerful acids, sulphur being precipitated, and sulphurous acid frequently evolved.

TETRATHIONIC ACID, S_4O_6 . *Eq. 104.*—On dissolving iodine in hyposulphuric acid, iodide of barium and tetrathionate of baryta are formed, as is shown by the following equation:—



The tetrathionate of baryta is insoluble in strong alcohol, and may therefore be separated from the admixture of iodine and iodide of barium. An aqueous solution of the acid may be obtained by carefully decomposing the baryta-salt with sulphuric acid.

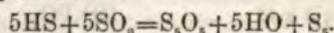
Properties.—The solution of tetrathionic acid is transparent and colorless; it is decomposed by heat into sulphur, sulphurous and sulphuric acids:—



Nitric acid decomposes it, but hydrochloric and sulphuric acids do not. In contact with a strong base, this acid sometimes decomposes into trithionic acid and sulphur.

The salts of tetrathionic acid may be best obtained in the crystalline state by mixing their aqueous solutions with alcohol. They are decomposed by heat into the trithionates.

PENTATHIONIC ACID, S_5O_6 . *Eq. 120.*—This acid is produced by the action of hydrosulphuric and sulphurous acids upon each other; water being simultaneously formed, and sulphur deposited:—



An aqueous solution is obtained by passing excess of hydrosulphuric acid into a saturated solution of sulphurous acid, digesting the filtered solution with copper until it is perfectly clear, separating the dissolved copper from the solution by hydrosulphuric acid, and expelling the excess of the latter by boiling.

Properties.—The solution of pentathionic acid is colorless and inodorous; it does not decompose at ordinary temperatures, and a weak solution may be concentrated by the aid of heat, without decomposition, until it attains a specific gravity of 1.37, when it is decomposed, hyposulphurous, sulphurous, and sulphuric acids being formed, and sulphur deposited. Oxidizing agents convert it into sulphuric acid.

But little is known respecting the pentathionates; they are very unstable, being the fifth equivalent of sulphur existing, apparently, but very loosely combined with oxygen; frequently, strong solutions of pentathionates resolve themselves into the more stable tetrathionates, with deposition of sulphur; it is, therefore, very difficult to obtain the pentathionates in a solid form, even by evaporation of their solutions *in vacuo*.

SULPHUR AND HYDROGEN.

PENTASULPHIDE OF HYDROGEN, OR HYDROSULPHUROUS ACID.

HS₅. Eq. 81.

§ 108. *Preparation.*—When solutions of alkalis or alkaline earths are boiled with excess of sulphur, the metallic pentasulphides are obtained, together with the hyposulphites. Upon gradually adding a clear solution of a pentasulphide thus prepared (which is of a deep orange color) to a great excess of moderately strong hydrochloric acid (one of concentrated acid to two of water), and rapidly stirring, a viscid, almost transparent, light yellow liquid separates, collecting at the bottom of the vessel. This liquid, which is the pentasulphide of hydrogen, generally contains an excess of sulphur, which is liberated by the decomposition of the hyposulphite by the acid.

Properties.—Pentasulphide of hydrogen is a light yellow, transparent, oily liquid, possessing a peculiar acrid, somewhat sulphurous odor, and a taste both sweet and bitter. It dissolves sulphur to a considerable extent, becoming viscid; its true composition has therefore never been quite satisfactorily established. It undergoes spontaneous decomposition when kept, being resolved into hydrosulphuric acid and sulphur; hence it gradually becomes viscid, and finally solid, when preserved; and if the decomposition is allowed to take place in sealed tubes, the hydrosulphuric acid is liquefied by its own pressure. Elevation of temperature accelerates this decomposition; it is however prevented, or considerably retarded, by the presence of acids. Several metals and metallic oxides, some sulphides, powdered charcoal, and several other substances, promote the decomposition of pentasulphide of hydrogen, which, in this respect, is very similar to the binoxide of hydrogen. It is inflammable, burning with a blue flame, and yielding sulphurous acid and water.

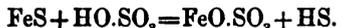
HYDROSULPHURIC ACID, SULPHURETTED HYDROGEN.

HS. Eq. 17. Sp. Gr. 1.1912.

Composition by Volume.—1 volume of sulphur-vapor and 6 volumes of hydrogen form 6 volumes of the gas.

Sulphuretted hydrogen occurs in nature in a great number of mineral and sulphurous springs; also in marshy districts, as a product of vegetable decomposition. It is always formed in the putrefactive decomposition of organic matters containing sulphur.

Preparation.—This acid is prepared by introducing some fragments of sulphide of iron (of the size of a small nut) into the generating vessel of a hydrogen-apparatus, provided with a washing-bottle (see § 27) containing a little water; the generating-bottle is half filled with water, and concentrated sulphuric acid gradually added, the bottle being slightly agitated after each fresh addition, so as to insure immediate mixture of the acid with the water. The production of the gas is as follows:—



The gas must be collected over a strong solution of salt, or hot water, or even over mercury, although the latter is slightly acted upon. When obtained in this manner, it frequently contains a little free hydrogen, carburetted hydrogen, &c.; a purer gas may be obtained, although in much smaller quantity, by heating powdered tersulphide of antimony with concentrated hydrochloric acid:—



This gas must be dried, if necessary, by means of chloride of calcium, since it decomposes oil of vitriol.

Properties.—Sulphuretted hydrogen is a colorless gas, possessing a peculiar odor (that of rotten eggs); it is highly poisonous, producing fainting and syncope when diluted with air, and acting as a narcotic poison when inhaled pure. It does not support combustion, but burns with a pale blue flame, the products being sulphurous acid and water:—



A little sulphuric acid is generally produced at the same time.

It reddens litmus-paper, but this reddening disappears on exposing the paper to the air. Sulphuretted hydrogen may be converted by a pressure of 17 atmospheres, into a transparent colorless liquid, which is far more mobile than ether, has the specific gravity 0.9, and dissolves sulphur with the aid of heat, depositing it again on cooling. At a temperature of -122°F. ($-85^\circ.7 \text{C.}$) sulphuretted hydrogen solidifies to a white crystalline translucent substance.

If sulphuretted hydrogen be passed through a redhot tube, it is decomposed, hydrogen escaping, and sulphur being deposited. A mixture of sulphuretted hydrogen and oxygen explodes upon the approach of flame, the products being water and sulphur, or sulphurous acid, according to the proportion of oxygen employed.

Sulphuretted hydrogen is oxidized with great facility by some acids and by a few high metallic oxides, these becoming converted into lower oxides. Thus, chromic acid is converted into sesquioxide of chromium, and sesquioxide of iron into oxide, by treatment with sulphuretted hydrogen, water being formed, and sulphur precipitated, oxides of sulphur being also sometimes produced.

When hydrosulphuric acid is passed into moderately strong nitric acid, its hydrogen is oxidized, and the greater portion of the sulphur separated in a peculiar viscid state. A little sulphate of ammonia is formed at the same time.

When passed through concentrated sulphuric acid, this gas is also decomposed, water and sulphurous acid being formed, and sulphur deposited. Chlorine, bromine, and iodine decompose sulphuretted hydrogen, the results being hydrochloric, hydrobromic, and hydriodic acids respectively, and sulphur. A few metals also decompose this gas when heated in it, the sulphides being produced and hydrogen evolved.

Sulphuretted hydrogen is soluble to a considerable extent in water, which absorbs about $2\frac{1}{2}$ times its own volume at ordinary temperatures; the solution possesses properties similar to those of the gas; it undergoes gradual decomposition on exposure to air and light, sulphur being deposited; it should, therefore, be kept in closely stoppered bottles, quite full. A hydrate of the acid may also be formed, existing only at low temperatures.

Sulphuretted hydrogen acts upon metallic oxides in solution, converting them into *sulphides* with formation of water. These compounds will be presently reverted to.

§ 109. SULPHUR AND NITROGEN.—By the action of water upon a substance produced by the combination of chloride of sulphur (S₂Cl₂) with ammonia, a light green solid is produced, which is a combination of sulphur with nitrogen, having the formula NS₂,¹ and which is decomposed by water into hyposulphurous acid and ammonia.

NITROSULPHURIC ACID.—A compound of sulphurous acid and binoxide of nitrogen called *sulphite of nitric oxide*, or *nitrosulphuric acid*, having the formula NO₂.SO₂, exists in combination with the alkaline bases, but cannot be obtained in the separate state.

The nitrosulphates are prepared by treating alkaline sulphites with nitric oxide. They are crystalline and colorless, their composition is represented by the formula, MO.NO₂.SO₂.

¹ Or, according to Fordos and Gélis, NS₂.

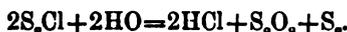
SULPHATE OF NITRIC OXIDE.—This substance is formed when dry binoxide of nitrogen is passed over anhydrous sulphuric acid as long as it is absorbed, or when liquid sulphurous and hyponitric acids are agitated together in a sealed tube. It is also formed by allowing dry sulphurous acid, binoxide of nitrogen and air to mix in a glass globe.

Properties.—This peculiar compound crystallizes in rectangular prisms, or in masses of white silky needles. Its spec. grav. is 2.14. It begins to fuse at 422°.6 F. (217° C.), and becomes quite fluid at 446° F. (230° C.); its boiling-point is nearly that of mercury; it distils without decomposition. It is rapidly decomposed by contact with water, nitric oxide being evolved, and hydrated sulphuric acid formed. This compound, or one very similar to it, has already been referred to, as obtained in the preparation of sulphuric acid in the absence of a sufficient amount of moisture; when exposed to the air, it deliquesces, forming a colorless liquid, which, however, gradually evolves red fumes, in consequence of the action of atmospheric moisture.

SULPHUR AND CHLORINE.

§ 110. **SUBCHLORIDE OF SULPHUR.**— S_2Cl . *Eq.* 67.5. *Sp. Gr.* 1.637. *Preparation.*—Dry chlorine gas is passed into a retort containing dried flowers of sulphur, until nearly the whole of the latter is converted; the subchloride is then distilled off from the excess of sulphur at a gentle heat.

Properties.—Subchloride of sulphur is a reddish-brown oily liquid, of a peculiar sweet but disagreeable and suffocating odor; it boils at about 280°.4 F. (138° C.); the spec. grav. of its vapor is 4.70. It is gradually decomposed by water, yielding hyposulphurous and hydrochloric acids and sulphur (perhaps also a small quantity of sulphuric acid):—



The hyposulphurous acid is soon decomposed into sulphur and sulphurous acid.

Subchloride of sulphur dissolves sulphur in considerable quantities, depositing it in the crystalline form, if allowed to evaporate spontaneously. This compound is employed in one of the processes for vulcanizing caoutchouc.

CHLORIDE OF SULPHUR, S_2Cl_2 . *Eq.* 51.5. *Sp. Gr.* 1.62.

Preparation.—Dry chlorine is passed in excess through sulphur, or the preceding compound; the resulting liquid is repeatedly distilled at a temperature of about 140° F. (60° C.) in a current of chlorine gas, which is passed into the liquid during the distillation.

Properties.—Chloride of sulphur is a dark red-brown somewhat mobile liquid, of a similar odor to the preceding substance, and fuming on exposure to air; its boiling point is 147°.2 F. (64° C.), and the spec. grav. of its vapor is 3.7. It is decomposed by water into hydrochloric and hyposulphurous acids:—



A small quantity of sulphuric acid is, however, simultaneously produced.¹ Chloride of sulphur is capable of dissolving phosphorus.

Two other chlorides of sulphur, the *bichloride* and *terchloride*, appear also to exist; there is, however, but little known respecting their nature. The terchloride forms two or three compounds with different proportions of sulphuric acid.²

¹ From recent experiments, it appears that some of the polythionic acids are also produced when the chlorides of sulphur are decomposed by water.

² Two compounds of ammonia with chloride of sulphur have been obtained, containing respectively, 1 and 2 eqs. of ammonia. When the former compound is exposed for some hours to a temperature of 212° in a sealed tube, it is converted into chloride of ammonium and a yellow solid of the formula NS_4Cl , which is termed *chlorosulphide of nitrogen*.

SULPHUR AND BROMINE.—Bromine dissolves sulphur, yielding an oily brownish-red liquid, rather darker than the preceding compounds; the amount of sulphur taken up by bromine at ordinary temperatures appears to be in the proportion of two equivalents to one equivalent of the latter; no really definite compounds have, however, been obtained. The bromides of sulphur appear to be analogous to the chlorides.

SULPHUR AND IODINE.—When sulphur and iodine are gently heated together, in the proportion of 1 part of sulphur to 7.9 parts of iodine, single equivalents, they combine and liquefy; the brown liquid solidifies on cooling to a blackish-gray crystalline mass of iodide of sulphur, SI ; it is insoluble in water, and is decomposed on exposure to air. It has met with medicinal application in cutaneous diseases.

METALLIC SULPHIDES.—The compounds of sulphur with metals are produced in various ways; they are sometimes formed by bringing the metals in contact with sulphur at ordinary or elevated temperatures. Some metals combine with sulphur when heated in its vapor, undergoing combustion analogous to their combustion in oxygen.

They may also be produced by exposing compounds of metallic oxides with the acids of sulphur to the action of reducing agents (*e. g.* hydrogen or charcoal) with the aid of heat; by igniting metallic oxides with sulphur, or exposing them to the vapor of bisulphide of carbon at a red heat; by decomposing metallic oxides or their salts by means of sulphuretted hydrogen or an alkaline sulphide. Many sulphides, particularly those containing large proportions of sulphur, occur in the mineral kingdom.

Metallic sulphides are solid, and generally crystalline; they present a greater variety of color and appearance than any other class of compounds; many possess a metallic lustre.

The sulphides of most heavy metals are insoluble in water; those of the metals of the alkalis and alkaline earths are, however, soluble; their solutions undergo gradual oxidation on exposure to air. Some sulphides part with their sulphur at a moderate heat; others require a high temperature for their decomposition, but are converted into oxides or metals, with evolution of sulphurous acid, by the action of air or oxygen with the aid of heat. Most sulphides are decomposed by the stronger acids (hydrochloric or sulphuric acid), sulphuretted hydrogen being evolved, and the metallic chlorides or sulphates formed. Chlorine decomposes many sulphides, yielding chlorides of sulphur and of the metals; nitric and nitro-hydrochloric acids convert them into oxides and sulphuric acid, a portion of sulphur being sometimes liberated. The sulphides obtained by precipitation with sulphuretted hydrogen, or alkaline sulphides, are generally hydrates, and frequently differ very considerably in color from the corresponding anhydrous sulphides; they lose their water when heated out of contact with air, and are easily oxidized at ordinary temperatures by the latter.

Some few metallic sulphides, containing large proportions of sulphur, may be considered to possess acid properties, inasmuch as they are capable of combining with certain anhydrous sulphides, *e. g.* As_2S_3 , SnS_2 , &c. or form acidic sulphides, *e. g.* As_2S_5 , SnS_4 , &c. Some sulphides also combine with metallic oxides, forming the so-called *sesquisulphides*.

SELENIUM.¹*Sym. Se. Eq. 39.5. Sp. Gr. 4.3.*

§ 111. This element was discovered by Berzelius, in 1817. It exists in small quantities in a great variety of minerals, especially in combination with lead, silver, copper, and mercury, and also with sulphur; it is found in small quantities in some varieties of iron pyrites, which yield on distillation seleniferous sulphur. In the use of sulphur obtained from these sources, for the preparation of sulphuric acid, a *seleniferous deposit* is formed on the floor of the leaden chamber.

Preparation.—Various methods are employed for obtaining selenium from its ores, or from the seleniferous deposit; these consist in the conversion of the selenium into selenious or selenic acid by oxidation with nitre or nitric acid, and their subsequent reduction by sulphurous acid.

Properties.—Selenium is obtained, by precipitation, as a red powder, which becomes semi-fluid at about 212° F. (100° C.), fusing perfectly at a somewhat higher temperature; it boils at about 1326° F. (700° C.); its vapor is yellow, somewhat darker in color than chlorine; it condenses to small dark drops of metallic lustre, or to a red crystalline powder (*flowers of selenium*), which is very inflammable, being converted into selenious acid.

On cooling after fusion, selenium remains soft for some time, so that it may be moulded into any form; after solidification, it appears as a brittle, nearly black, or leaden-gray mass, possessing considerable metallic lustre, and transmitting red light through very thin scales. When rapidly cooled, its surface appears red brown; its fracture is conchoidal. It may be crystallized in four-sided prisms.² Selenium is insoluble in water; it dissolves in concentrated sulphuric acid, imparting a green color to the liquid; water reprecipitates it from this solution. When heated in air, it produces a colorless gas, which possesses a very powerful odor, similar to that of horseradish;³ this compound is oxide of selenium, SeO. Oxygen also combines with this element to form selenious acid, SeO₂, and selenic acid, SeO₃. With hydrogen, it forms hydroselenic acid, HSe; it also unites with sulphur, phosphorus, chlorine, bromine, and with the metals, yielding selenides, which correspond to sulphides.

The relations of selenium to solvents are similar to those of sulphur, to which it is very analogous in most of its chemical characters.

SELENIUM AND OXYGEN.

Oxide of selenium	SeO
Selenious acid	SeO ₂
Selenic acid	SeO ₃

OXIDE OF SELENIUM, SeO. *Eq. 47.5.*

This oxide is formed, as already stated, by the combustion of selenium in air or oxygen (some selenious acid being simultaneously produced).

It is a colorless gas, possessing a peculiar odor, similar to that of horseradish;

¹ From *σταρα*, the moon.

² The analogy between sulphur and selenium, as regards their allotropic modifications, has been rendered evident by the recent experiments of Hittorf.

³ According to Sacc, this odor is due to the formation of a minute quantity of hydro-selenic acid; upon heating selenium in perfectly dry air, no odor whatever was observable.

It has no acid properties, and is but slightly soluble in water, to which it imparts its characteristic odor.

SELENIOUS ACID, SeO_2 . Eq. 55.5.

Preparation.—When selenium is burnt in air or oxygen, selenious acid is produced, besides the above oxide. It is generally obtained by dissolving selenium in warm nitric or nitromuriatic acid, and distilling the solution; the nitric and hydrochloric acids pass over first, and the selenious acid is left, subliming upon continued application of heat.

Properties.—Selenious acid is a solid, white, translucent substance, which may be obtained by sublimation in white four-sided needles, possessing a peculiar lustre.

Its vapor is yellow, somewhat resembling chlorine. It has an acid taste, and the vapor possesses a pungent odor. It is very soluble in cold water, and still more so in hot. Its concentrated hot aqueous solution deposits crystals of a hydrate, which in their appearance much resemble nitre.

Selenious acid and its salts are deoxidized by sulphurous acid, selenium being precipitated in dark red flakes:—



The decomposition is much accelerated by heat. A solution of selenious acid, containing an admixture of some powerful mineral acid (hydrochloric or sulphuric acid), is decomposed on the introduction of iron, zinc, silver, and several other metals, the selenium being deposited in the form of a red-brown film. Selenious acid is also decomposed by hydrosulphuric acid, with formation of bisulphide of selenium and water:—



Selenious acid possesses considerable affinity for bases, with which it forms selenites.

SELENIC ACID, HO.SeO_3 . Eq. 72.5.

Preparation.—This acid is formed by fusing selenium, or metallic selenides, with nitre; seleniate of potassa is thus obtained: this is dissolved in water, and a solution of nitrate of lead added: seleniate of lead is precipitated, which is well washed, then suspended in water, and decomposed by hydrosulphuric acid. The solution of selenic acid is separated by filtration from the sulphide of lead, and concentrated by gentle evaporation, until its specific gravity is about 2.6. In this state it has nearly the composition of anhydrous selenic acid, HO.SeO_3 . If evaporated further, it undergoes decomposition.

Properties.—Selenic acid exists in the anhydrous state. The concentrated solution is transparent and colorless: it bears great resemblance to sulphuric acid.

When heated above 343°F (173°C) it decomposes into selenious acid and oxygen. Hydrosulphuric acid also decomposes it with the aid of heat: chlorine is evolved and selenious acid produced.

The mixing concentrated sulphuric acid with water, nearly as much heat is evolved as in the dilution of nitric acid.

The affinity of selenium and its bases is nearly equal to that of sulphuric acid. The oxides correspond to and are isomorphous with the sulphates. The neutral salts are all soluble in water, excepting those of oxide of iron, barium, and strontium. The oxides form white chlorides, selenates, and selenides being generally insoluble. They are reduced by hydrogen or sulphur. When treated with hydrochloric acid, they are converted into selenious acid, being converted.

SELENIUM AND HYDROGEN.

HYDROSELENIC ACID, SELENIURETTED HYDROGEN.

HSe. Eq. 40.5. Sp. Gr. 3.42.

§ 112. *Preparation*.—Upon adding hydrochloric acid or dilute sulphuric acid to selenide of potassium or of iron, hydroselenic acid is disengaged:—



It must be collected over mercury.

Properties.—Seleniuretted hydrogen is a colorless gas, possessing an odor very like that of sulphuretted hydrogen; it is even more poisonous than the latter; it produces a very painful sensation and irritation in the mucous membrane of the nose and eyes; it destroys the sense of smell for some time, and frequently brings on a bad cough, lasting for some days. It is inflammable, burning with a blue flame, oxide of selenium and selenious acid being produced, and selenium deposited.

Hydroselenic acid is absorbed by water even more plentifully than hydrosulphuric acid; the solution is colorless, and has a faint odor. It is gradually decomposed, like hydrosulphuric acid, in contact with air; selenium being deposited in dark-red flakes.

When a solution of seleniuretted hydrogen is added to (or the gas passed through) solutions of most of the heavy metals, *selenides* are precipitated; most of them are either dark brown or black; the salts of cerium, manganese, and zinc, however, give flesh-colored precipitates.

SELENIUM AND CHLORINE.—The action of chlorine on selenium gives rise to the production of two compounds; when chlorine is passed over selenium, the latter melts, considerable heat being disengaged, and a brown liquid formed; if the action of chlorine be continued, this liquid is converted into a white solid.

The first of these products is the *subchloride of selenium*, Se_2Cl . It is an oily, transparent, brown, volatile liquid, heavier than water, which decomposes it gradually into hydrochloric and selenious acids, and selenium.

Bichloride of Selenium, SeCl_2 , is the white substance above referred to, produced by the action of excess of chlorine upon the subchloride. It is more volatile than the latter, and sublimes in white crystals. When it is brought in contact with water, a slight effervescence ensues, accompanied by disengagement of heat and its conversion into selenious and hydrochloric acids. By treating the bichloride with a fresh quantity of selenium, it is reconverted into the subchloride.

SELENIUM AND BROMINE.—There appear to be several compounds of selenium and bromine; but that in which these elements are found in the proportion of five of the latter to one of the former, appears to be the most stable.

SELENIUM AND SULPHUR.—These two substances may be made to mix in all proportions by fusing them together. Two definite combinations of selenium and sulphur have, however, been obtained; the *bisulphide* and the *tersulphide* of selenium.

Bisulphide of Selenium, SeS_2 , is produced by passing hydrosulphuric acid into a solution of hydroselenic acid; a yellow precipitate is formed, which collects to a red mass when the liquid is heated.

The Tersulphide of Selenium, SeS_3 , is formed when three equivalents of sulphur and one of selenium are fused together.

METALLIC SELENIDES are prepared artificially by methods similar to those which furnish the sulphides, to which they are analogous in their properties. The selenides of the alkaline metals are red, or red-brown; those of the other

metals (with the exceptions before mentioned) are dark-colored, and possess a certain metallic lustre. When heated in air they are decomposed, though not so rapidly as the sulphides; the selenium burns away with a reddish-blue flame. Some selenides, like the sulphides, exist in combination with water. The alkaline selenides are soluble in water; they generally possess a reddish tinge, owing doubtless to excess of selenium, as they soon decompose on exposure to air; when mixed with acids they evolve hydroselenic acid.

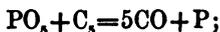
PHOSPHORUS.¹

Sym. P. Eq. 32.² Sp. Gr. 1.77.

§ 113. This element was discovered by Brandt, in 1669, who obtained it by distilling the residue of urine; the first method of preparing it was published by Künckel.

Phosphorus occurs, in combination with oxygen and metallic oxides, in the bones of animals, in urinary and other excrements, and in many portions of the vegetable creation. It exists in fibrin and albumen, both animal and vegetable. In the mineral kingdom it occurs as phosphoric acid, in combination with lime (as apatite), alumina (wavellite), lead, copper, &c., and also in meteoric iron. It likewise is found occasionally in marshy districts, as phosphuretted hydrogen (resulting from vegetable or animal decay).³

Preparation.—In order to obtain phosphorus, bones, which consist almost entirely of gelatin and phosphate of lime, are calcined in open vessels until the former is entirely burnt away. The bone ash thus obtained is then reduced to powder; 3 parts of this ash, 2 parts of oil of vitriol, and 16 parts of water, are intimately mixed and digested together for some considerable time; the liquid, which then contains acid phosphate of lime, is separated by straining through linen from the insoluble sulphate of lime, concentrated to a thick syrup, and afterwards mixed with $\frac{1}{4}$ part of charcoal, when it assumes a doughy consistence. The mass is then strongly heated in an iron vessel, being kept constantly stirred until perfectly dry, and afterwards transferred, when cool, as rapidly as possible, into an iron or stoneware retort, to the neck of which is adapted a wide tube, bent at right angles, and passing to the bottom of a receiver containing water, and provided with an outlet for the gaseous products. The receiver should also be surrounded with water. The phosphoric acid is acted upon by the charcoal in the following manner:—⁴



but only the excess of phosphoric acid contained in the acid phosphate of lime is acted upon by the charcoal, ordinary phosphate of lime being left in the retort. The phosphorus is condensed by the water in the receiver, as it distils over; the carbonic oxide evolved is generally mixed with some phosphuretted hydrogen, in consequence of the presence of a small quantity of water in the mixture, which undergoes decomposition, the hydrogen uniting with a portion of the

¹ φῶς, light, φέρειν, to bear.

² Berzelius, 31.6; Schrötter, 31.

³ Nearly all soils contain phosphorus in the form of phosphoric acid, but in very minute proportions; the plants which grow upon these soils contain it in larger quantities, since they have as it were concentrated it within their tissues; the animals which live upon such plants contain the largest proportion of phosphorus, and hence they form the source from which this element is prepared.

⁴ A modification of the above process has been proposed by Wöhler, which consists in adding to the mixture of acid phosphate and charcoal, a quantity of sand (silicic acid), which combines with the lime, thus liberating the whole of the phosphoric acid.

phosphorus. This gas being spontaneously inflammable, there is some little risk of explosion attending the preparation of phosphorus, unless the mixture has been most carefully dried. After the phosphorus has distilled over, it is melted under warm water and pressed through chamois leather, by which process it is freed from adhering charcoal and red oxide of phosphorus; it is then once more melted, and introduced into glass tubes, closed at one end with a cork. When the phosphorus is cool, it is easily pushed out in the form of a stick. Phosphorus must be preserved under water in a tightly-closing vessel; it is also advisable to keep it in the dark.

Properties.—Phosphorus is, when pure, a colorless, or faintly yellow, transparent, or semi-opaque solid, possessing the appearance and consistence of wax. It crystallizes in regular octohedra and rhomboidal dodecahedra. It fuses at 113° F. (45° C.), becoming a transparent oily liquid, which frequently may be cooled down far below the melting point without solidifying, as it does, however, the moment it is brought into contact with a solid substance. The boiling point of phosphorus is 554° F. (290° C.); its vapor is colorless, and possesses a density of 4.355. It volatilizes at far below its boiling point, and is even slightly volatile at ordinary temperatures. Phosphorus is itself devoid of taste or smell, but when exposed to the air it undergoes a slow combustion, appearing luminous in the dark, and giving off white vapors, which consist of phosphorous acid (said to be mixed with phosphoric acid), at the same time emitting a peculiar odor, something like garlic.¹ This smell is partly owing to the production of ozone (see § 72). Phosphorus is insoluble in water, but soluble in alcohol, ether, bisulphide of carbon, essential oils, and terchloride of phosphorus. When in solution it has an acrid, unpleasant taste; it acts as a violent irritant poison.

Phosphorus is highly inflammable; when heated in air it soon takes fire, burning with a white brilliant light, and evolving white vapors consisting of phosphoric acid. A piece of wood or paper cannot easily be kindled in the flame of phosphorus, since the phosphoric acid condenses upon its surface, thus protecting it from the action of the flame. When dry, phosphorus may also inflame spontaneously, especially in warm weather, or if repeatedly handled; it is therefore necessary to manipulate with this substance under water; or, if this be impracticable, the hands and phosphorus should both be immersed in cold water from time to time.

The inflammability of phosphorus is much increased when it is in a finely divided state; this is well seen if some phosphorus be dissolved in bisulphide of carbon at a very gentle heat, and the solution poured upon a piece of filtering-paper. The bisulphide of carbon evaporates rapidly, leaving a thin film of phosphorus upon the surface, which inflames as soon as the paper is dry. Phosphorus may also be kindled by friction, or percussion.

Phosphorus is capable of existing in three modifications, differing from each other to a considerable extent in many of their properties, though identical in their chemical character. These are—1st, the ordinary phosphorus, the properties of which have just been described; 2d, white phosphorus; and 3d, red, or amorphous phosphorus. The two latter are termed allotropic² modifications of phosphorus.

White Phosphorus.—If phosphorus be exposed under water, to sunlight, or diffused daylight, it becomes coated, after a time, with a white opaque crust, the

¹ This gradual oxidation of phosphorus may be prevented by the presence of a small quantity of olefiant gas, ether-vapor, or some essential oil; in fact, it is said that phosphorus may be distilled in an atmosphere containing a considerable quantity of turpentine-vapor. In pure oxygen, at a temperature of 60° F. (15° C.), no oxidation of phosphorus takes place; it commences at once, however, if the gas be rarefied, or diluted with hydrogen, nitrogen, or carbonic acid.

² See § 103.

specific gravity of which is 1.515. It may be dried without alteration over oil of vitriol, but is converted into ordinary phosphorus at a temperature even below 122° F. (50° C.), unaccompanied by loss of weight or production of water, showing that this white substance is only phosphorus in an altered state of aggregation.

Red, or Amorphous Phosphorus.—This modification of phosphorus is likewise produced by the action of light on the ordinary modification, under water or alcohol, or in carbonic acid and gases containing no oxygen; it was formerly regarded as an oxide of phosphorus. Berzelius was the first to consider it as allotropic phosphorus. It has recently been more completely examined by Schrötter, who has found that it may be readily obtained by exposing phosphorus, for a length of time, in an atmosphere free from oxygen or moisture, to a temperature ranging between 464° and 482° F. (240° and 250° C.); the fused phosphorus, which at first is transparent and colorless, will gradually become red and opaque, and may be finally freed from any small portion of ordinary phosphorus by digestion in bisulphide of carbon, in which this amorphous modification is perfectly insoluble.

When dry, amorphous phosphorus is a scarlet, or carmine, lustreless powder, which becomes darker when heated. It is also obtained on the large scale in dark dense masses of a red, and sometimes blackish-brown color.

Its specific gravity is 1.964 at 50° F. (10° C.) It does not become luminous in the dark until heated to a temperature closely approaching that at which it inflames (500° F. 260° C.); and, under all circumstances, this substance is much less inflammable than ordinary phosphorus. It is insoluble in most of the solvents for phosphorus, and has been found devoid of the poisonous properties of that substance in its ordinary condition.

When distilled in an atmosphere of carbonic acid at a temperature of 500° F. (260° C.), it is reconverted into ordinary phosphorus.

Phosphorus combines with oxygen to form suboxide of phosphorus, P_2O , hypophosphorous acid, PO , phosphorous acid, PO_2 , and phosphoric acid, PO_3 ; with hydrogen it forms three peculiar compounds (which will be subsequently described); it also forms compounds with nitrogen, chlorine, bromine, iodine, sulphur, and selenium.

The affinity of phosphorus for the metals is inferior to that of sulphur. The compounds it forms are termed phosphides (phosphures), and are somewhat analogous to the sulphides.

The phosphorus of commerce frequently contains arsenic and sulphur. In order to detect these impurities, the phosphorus may be heated with moderately concentrated nitric acid (when arsenic is sometimes left as a black powder); the nitric solution is evaporated nearly to dryness, and divided into two parts—one to be tested for arsenic by boiling with sulphate of ammonia, evaporating to expel sulphurous acid, and passing sulphuretted hydrogen, when the yellow sulphide of arsenic will be precipitated—the other portion is diluted considerably with water, and tested with chloride of barium, in the presence of hydrochloric acid; if a white precipitate of sulphate of barium is obtained, the presence of sulphur in the phosphorus may be inferred.

Use of Phosphorus.—This element is extensively used for the manufacture of lucifer matches for which the red modification has of late been employed, since it is less dangerous to handle, and is not so liable to spontaneous inflammation. Phosphorus is also sometimes employed in small quantities medicinally; and in chemistry it is generally used as a reagent for arsenic, as a poison for rats, &c.

PHOSPHORUS AND OXYGEN.

Suboxide of phosphorus . . .	P_2O		Phosphorous acid	PO_3
Hypophosphorous acid . . .	PO	.	Phosphoric acid	PO_5

SUBOXIDE OF PHOSPHORUS, P_2O . *Eq. 72.*

§ 114. *Preparation.*—This compound is produced by throwing a stream of oxygen upon phosphorus fused under water. Vivid flashes of light are produced, and some phosphoric acid is simultaneously formed; this, being soluble in water, may be easily separated, by washing, from the pulverulent suboxide of phosphorus, which is dried over oil of vitriol. Any unoxidized phosphorus may be extracted by means of bisulphide of carbon.

Properties.—Suboxide of phosphorus is a red powder, which is insoluble in ether, alcohol, volatile and fixed oils; and, when heated in close vessels, is converted into phosphoric acid, and phosphorus:—



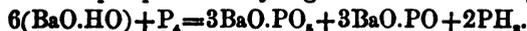
If heated nearly to redness in air, it takes fire, being converted into phosphoric acid; it oxidizes gradually when moist, or in damp air; it takes fire in chlorine, and also when brought into contact with nitric acid, by which it is immediately converted into phosphoric acid. It is also decomposed by solutions of the alkalis, hypophosphite of the alkali, and phosphuretted hydrogen being produced.

A hydrate of this suboxide also exists, but cannot be preserved, since it parts with its water, yielding the red suboxide, directly an attempt is made to dry it, even at ordinary temperatures. It is a yellow substance, slightly soluble in water.

HYPOPHOSPHOROUS ACID, PO . *Eq. 40.*

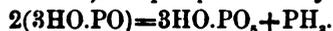
Preparation.—When the phosphides of the alkaline metals, or of barium, strontium and magnesium, are acted upon by water, hypophosphites are produced. It may also be obtained by boiling phosphorus with aqueous solutions of the alkalis, milk of lime, or baryta-water.

Phosphoric acid and phosphuretted hydrogen are simultaneously produced:—



The best method of obtaining a solution of the acid consists in boiling phosphorus with baryta-water in an open wide-mouthed flask, and separating the precipitated phosphate of baryta by filtration; a slight excess of sulphuric acid is added to the solution to separate the baryta, the filtered liquid digested with oxide of lead in the cold, filtered, and the clear solution of hypophosphite of lead thus produced, decomposed by hydrosulphuric acid; the liquid is then freed from sulphide of lead by filtration, and concentrated by evaporation.

Properties.—Hypophosphorous acid does not exist in the anhydrous state; upon concentrating the aqueous solution, a very acid, viscid liquid is obtained, which is a hydrate of the acid, of the formula, $3HO.PO$. When heated, it is decomposed into phosphoric acid, and phosphuretted hydrogen gas:—



Hypophosphorous acid is a powerful reducing agent, being easily converted into phosphoric acid at the expense of the oxygen contained in the other substance. This acid appears to be tribasic.

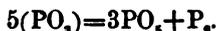
The *hypophosphites* are, most of them, crystallizable, and appear to exist combined with a certain amount of water. When heated, they are decomposed into phosphates and phosphuretted hydrogen (a little suboxide of phosphorus appears likewise to be produced). These salts are all soluble in water, and some are soluble in alcohol; they are converted into phosphates by boiling in contact with air.

PHOSPHOROUS ACID, PO_2 . *Eq. 56.*

This acid is produced by the slow and imperfect combustion of phosphorus.

Preparation.—The anhydrous acid is obtained by heating phosphorus gently in a narrow glass tube, drawn out to a long narrow point, through which a very slow stream of dry air is passed; the acid forms a white sublimate in the anterior part of the tube; phosphoric acid and suboxide of phosphorus are simultaneously formed.

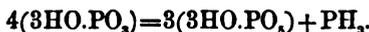
Properties.—Phosphorous acid forms white bulky flakes, deliquescing in damp air. It is capable of being sublimed, and does not redden dry litmus-paper. When heated in close vessels, it is converted into anhydrous phosphoric acid and phosphorus:—



The hydrate, $\text{PO}_2 \cdot 3\text{HO}$, is prepared by decomposing the terchloride of phosphorus by water:—



The hydrochloric acid simultaneously produced is expelled by a gentle heat, and the solution of acid concentrated, until it yields a mass of deliquescent crystals; if evaporated still further (*in vacuo*), it yields a thick uncrystallizable syrup. When heated in this state, it is decomposed into phosphoric acid, phosphuretted hydrogen, and water:—



Phosphorous acid also acts as a reducing agent, on account of its affinity for oxygen. It may be detected in the water under which phosphorus has been kept for some time, by testing with solution of nitrate of silver, when a black precipitate of metallic silver is obtained.

Phosphorous acid is a tribasic acid; it does not possess very powerful affinities for bases.

The *phosphites* appear always to exist in combination with water. Some are soluble in the latter, and those which are insoluble may be dissolved in the presence of excess of acid. Phosphites are not oxidized by exposure to air at ordinary temperatures; they are, however, converted into phosphates by chlorine, nitric acid, and many metallic oxides. Solutions of these salts produce no precipitate in a mixture of chloride of ammonium, ammonia, or sulphate of magnesia, whereby they are easily distinguished from phosphates.

Another acid, intermediate between phosphorous and phosphoric acid has been described by Pelletier, to which the names *hypophosphoric acid* and *phosphatic acid* have been given.

It is also formed by the slow combustion of phosphorus, and is prepared by introducing sticks of phosphorus into tubes elongated at the bottom, and placed side by side in a funnel, the neck of which dips in a bottle placed in a vessel containing water; this arrangement should be kept in a cool place, and the mouth of the funnel should be partly covered with a glass plate.

The acid drops into the bottle as it is formed; it appears as a syrupy liquid, possessing a faint garlic smell.

The composition of this acid is not thoroughly established; it appears to possess the formula P_2O_6 , being intermediate between phosphorous and phosphoric acids.

PHOSPHORIC ACID (*anhydrous*), PO_5 . *Eq. 72.*

§ 115. Phosphoric acid is found abundantly in the mineral kingdom, in combination with various metallic oxides, as already mentioned. It exists in several *igneous rocks*, and in all rocks of primitive origin. It is also found in the animal

kingdom, as phosphates of lime, magnesia, and ammonia, and in the ashes of many plants.

ANHYDROUS PHOSPHORIC ACID is produced by the rapid combustion of phosphorus in dry air or oxygen. It is thus obtained in white light flakes, which fuse to a vitreous mass at a red heat, and sublime at a still higher temperature. It does not appear to possess acid properties, until it has combined with water. It unites with the latter with great energy, a hissing noise being produced when water is dropped upon it; it does not, however, disappear immediately, but forms a flocculent hydrate, which gradually dissolves.

It is decomposed by charcoal at a red heat, and also by potassium, sodium, iron, and some other metals, phosphides of the metals and phosphates of the metallic oxides being generally produced.¹

HYDRATES OF PHOSPHORIC ACID.—There exist three different hydrates of phosphoric acid (besides modifications of these lately discovered). Several views are taken of the true constitution of these hydrates, which differ remarkably from each other in their properties. They are considered either as anhydrous phosphoric acid in combination with various proportions of water, or, according to the theory of hydrogen-acids, as perfectly different compounds of the formulæ PO_6H , PO_7H_2 , PO_8H_3 . Though the latter view affords a better explanation of the properties and constitution of these acids, the former is still generally adopted among chemists. These acids are termed *mono-*, *bi-* and *tri-basic* phosphoric acids, or *metaphosphoric*, *pyrophosphoric*, and *common phosphoric acids*.

MONOBASIC, OR METAPHOSPHORIC ACID, HO.PO_3 .

This acid is formed by adding water to the anhydrous acid. It is best obtained by the following process: 1 part of phosphorus is cut into small pieces, and introduced into a retort connected with a receiver, and containing 13 parts of nitric acid, spec. grav. 1.2; the retort is moderately heated on a sand-bath, and the nitric acid which distils over returned to it from time to time, until the phosphorus has disappeared; the greater part of the nitric acid is then distilled off, and the residual liquid evaporated in a platinum capsule as long as any water is evolved; upon cooling, the phosphoric acid appears as a colorless glass (frequently termed *glacial* phosphoric acid), which dissolves slowly in water, and is volatilized to some extent when heated to redness. The acid obtained by this method sometimes contains traces of arsenic, which may be detected by Reinsch's test (*see* Analysis).

A solution of this acid may be also obtained by preparing the metaphosphate of lead from the soda-salt, produced by igniting ammonio-phosphate of soda, microcosmic salt ($\text{NaO.NH}_4\text{O.HO.PO}_3$), decomposing the lead-salt by means of hydrosulphuric acid, and heating the solution, separated from the sulphide of lead, to expel the excess of the gas.

The solution of this acid gives, with nitrate of silver, a white crystalline precipitate; it also coagulates albumen, and forms a difficultly-soluble salt when mixed with a solution of potassa. If kept for some days, or when boiled for some time, it combines with an additional equivalent of water, forming pyrophosphoric acid, and afterwards passes into ordinary or tribasic phosphoric acid. The water of hydration of this acid cannot be expelled by heat.

Metaphosphoric acid forms with bases only one class of salts, having the general formula MO.PO_3 . The soluble metaphosphates have a slightly acid reaction. They yield a white precipitate with nitrate of silver.

[The behavior of metaphosphoric acid with bases under various circumstances has been submitted to close examination by Maddrell, Henneberg, and Fleitmann.

¹ The powerful affinity of anhydrous phosphoric acid for water renders it very useful as a dehydrating agent; it is especially employed in organic investigations.

The last-named chemist has come to the conclusion that there exist five polymeric modifications of metaphosphoric acid, which he distinguishes as follows:—

Mono-metaphosphoric acid	PO_5, HO
Di-metaphosphoric acid	$2\text{PO}_5, 2\text{HO}$
Tri-metaphosphoric acid	$3\text{PO}_5, 3\text{HO}$
Tetra-metaphosphoric acid	$4\text{PO}_5, 4\text{HO}$
Hexa-metaphosphoric acid	$6\text{PO}_5, 6\text{HO}$

The following is his view regarding the formation of these various modifications: *Mono*-metaphosphoric acid is produced when equal equivalents of potassa and metaphosphoric acid are united together; *di*-metaphosphoric acid is formed when equal equivalents of metaphosphoric acid and protoxide of copper, zinc, or manganese, are heated together; *tri*-metaphosphoric acid is only produced when a mixture of equal equivalents of metaphosphoric acid and soda is allowed to crystallize by gradual cooling; *tetra*-metaphosphoric acid is obtained by the action of teroxide of bismuth and the protoxides of lead and cadmium upon metaphosphoric acid; and *hexa*-metaphosphoric acid is produced by igniting the hydrate of phosphoric acid, by rapidly cooling the fused soda-salt, and also by the action of protoxide of silver.]

PYROPHOSPHORIC ACID, $2\text{HO}.\text{PO}_5$.

If tribasic phosphoric acid is evaporated in a platinum vessel until the temperature reaches 415°F . (213°C .), it is converted into pyrophosphoric acid, which, when concentrated, forms a soft viscid glass, very soluble in water. A solution of this acid may be obtained by precipitating pyrophosphate of soda ($2\text{NaO}.\text{PO}_5$) with acetate of lead, diffusing the washed precipitate through water, decomposing it with hydrosulphuric acid, and freeing the filtered solution from the latter by evaporation. A solution of this acid does not coagulate albumen nor precipitate the chlorides of barium and calcium, and yields (only upon neutralising with ammonia) a white flaky precipitate with nitrate of silver. A solution of this acid may be preserved for some time in the cold, but is converted by heat into tribasic phosphoric acid.

Pyrophosphoric acid forms two classes of salts with metallic oxides; the acid pyrophosphates, $\text{MO}.\text{HO}.\text{PO}_5$, and the neutral pyrophosphates $2\text{MO}.\text{PO}_5$. The latter salts possess a slightly alkaline reaction. When a pyrophosphate is heated with excess of base, it is converted into a tribasic phosphate.

TRIBASIC, OR ORDINARY PHOSPHORIC ACID.

$3\text{HO}.\text{PO}_5$.

Preparation.—It has already been stated that when solutions of the preceding acids are heated for some time, they are converted into ordinary phosphoric acid. This acid may therefore be prepared by burning phosphorus gradually in air, under a bell jar, heating the resulting product with nitric acid, to convert any oxide of phosphorus or phosphorous acid into phosphoric acid, expelling the nitric acid by evaporation, and dissolving the resulting glacial mass in hot water.

A method commonly used for preparing this acid, is to decompose the acid phosphate of lime (obtained according to the method given in the preparation of phosphorus) with ammonia and carbonate of ammonia, the former of which decomposes the acid phosphate of lime, while the latter precipitates the lime from the sulphate.

The solution containing phosphate and sulphate of ammonia is evaporated to dryness and the residue ignited, when both the salts are decomposed, and glacial phosphoric acid remains; if this be boiled with water, it gives the tribasic acid. It is said that the phosphoric acid thus prepared always contains a little ammonia.

Properties.—If a solution of ordinary phosphoric acid be evaporated to a thin syrup, hard transparent crystals of trihydrate of phosphoric acid are obtained. Tribasic phosphoric acid parts with its water very slowly at 320° F. (160° C.) If heated for some time to 415° F. (213° C.), it loses one equivalent of its basic water, becoming converted into pyrophosphoric acid, 2HO.PO₃; at a red heat it loses a second equivalent, becoming metaphosphoric acid, HO.PO₃. A solution of tribasic phosphoric acid does not coagulate albumen, nor does it precipitate a solution of nitrate of silver; but when a small quantity of ammonia is added, a yellow precipitate of tribasic phosphate of silver is obtained.

Ordinary phosphoric acid forms with bases three different classes of salts; the neutral tribasic phosphates of the formula 3MO.PO₃; the common phosphates containing two equivalents of base, and one of basic water, to one of acid, 2MO.HO.PO₃; and the acid tribasic phosphates, containing one equivalent of base, and two of basic water, to one equivalent of acid, MO.2HO.PO₃. The neutral tribasic phosphates of the alkalies have a strongly alkaline reaction; the common phosphates of the alkalies are feebly alkaline; when ignited they are converted into pyrophosphates; the acid phosphates are converted by ignition into metaphosphates.

The different equivalents of basic water of tribasic phosphoric acid, may be replaced by equivalents of different bases. All soluble tribasic phosphates yield a yellow precipitate with nitrate of silver.

Fleitmann and Henneberg have discovered two new classes of phosphates, in which the base is combined with acid according to the formulæ, 3MO.2PO₃, and 6MO.5PO₃.

The soda-salts of these series will be described in the article upon soda.

Liebig considers the relations between the different modifications of phosphoric acid to be exhibited in the most simple manner, by regarding the composition of their salts in such a light as to compare quantities of these containing an equal amount of base; the following table would represent the general formulæ of the various phosphates according to this view:—

3MO.PO ₃	Common, or tribasic phosphates . . .	6MO.2PO ₃
2MO.PO ₃	Pyrophosphates	6MO.3PO ₃
3MO.2PO ₃	Fleitmann and Henneberg's new phosphates	6MO.4PO ₃
6MO.5PO ₃		6MO.5PO ₃
MO.PO ₃	Metaphosphates	6MO.6PO ₃

PHOSPHORUS AND HYDROGEN.

Solid phosphuretted hydrogen	P ₂ H
Liquid phosphuretted hydrogen	P H ₂
Gaseous phosphuretted hydrogen	P H ₃

SOLID PHOSPHURETTED HYDROGEN, PHOSPHIDE OF HYDROGEN. P₂H.

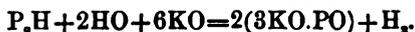
§ 116. Upon decomposing by water the phosphide of potassium, formed by fusing phosphorus and potassium together under naphtha, a yellow powder precipitates, which has been shown to be the solid phosphide of hydrogen.

This substance may also be produced in other ways; first, by exposing the phosphuretted hydrogen gas, obtained by heating phosphorus with milk of lime, to strong daylight, in bottles with the necks immersed in water. Yellow flakes are deposited after a time, the gas losing the spontaneous inflammability which it at first possessed. Secondly, it may be obtained by acting upon phosphide of calcium (Ca₃P) with strong hydrochloric acid, phosphuretted hydrogen gas being simultaneously produced. In both of these cases it appears that a second com-

pound, the liquid phosphide of hydrogen, to be presently described, is produced, which resolves itself into gaseous and solid phosphides, according to the following equation:—



Properties.—This substance, when freshly prepared, is yellow, but assumes an orange color by exposure to light; it is inodorous, not luminous in the dark, and takes fire at 392° F. (200° C.), and also when struck with a hammer upon an anvil. It is decomposed by water in the presence of an alkali, with the evolution of hydrogen, and the formation of a hypophosphite:—



In decomposing phosphide of calcium by water, a greenish substance is frequently observed, which appears to be isomeric with this solid phosphide.

LIQUID PHOSPHIDE OF HYDROGEN, PH_3 .

This compound is obtained by passing the gas evolved by the action of water on phosphide of calcium at 140° F. (60° C.), through an U-shaped tube immersed in a freezing mixture.

It is a colorless liquid, which does not solidify at -4° F. (-20° C.), but which is volatilized and decomposed at a temperature of 86° F. (30° C.); it is insoluble in water, and refracts light powerfully. It is resolved, by the action of light, into solid and gaseous phosphides of hydrogen.

Alcohol and oil of turpentine appear to dissolve it, but immediately decompose it in the above manner. It takes fire spontaneously on exposure to air, burning with a bright light. When mixed in the smallest proportion with phosphuretted hydrogen, carbonic oxide, hydrogen, or any other inflammable gas, it renders them spontaneously inflammable.

GASEOUS PHOSPHIDE OF HYDROGEN, PHOSPHURETTED HYDROGEN GAS.



Composition by Volume.—1 volume of phosphorus and 6 volumes of hydrogen condensed into 4 volumes.

This gas may be obtained in a state of purity by heating crystallized phosphorous acid in a green glass retort (if a white glass retort be employed the gas will contain a little free hydrogen, an alkaline phosphite being produced by the action of the phosphorous acid on the glass).

Hydrated phosphorous acid is decomposed according to the following equation:—



It may also be obtained as already stated, together with the solid compound, by acting upon phosphide of calcium with concentrated hydrochloric acid:—



When prepared by either of these methods, this gas is colorless, possessed of a disagreeable alliaceous odor, and is not spontaneously inflammable, but burns when a light is applied to it, being converted into water and phosphoric acid. A slight admixture of air, though producing no effect at first, will sometimes cause it to explode spontaneously after a time. It is slightly soluble in water.

Gaseous phosphuretted hydrogen may also be obtained in a spontaneously inflammable state, by boiling phosphorus together with water and hydrate of lime, or with a strong solution of potassa. A small flask is filled to about three-fourths with the solution of potassa (or milk of lime), a few fragments of phos-

phorus are introduced, and the flask heated on a sand-bath. As soon as the gas evolved burns at the mouth, a delivery-tube is attached, and the phosphuretted hydrogen collected over water. When a bubble is allowed to escape into the air, it will inflame with a slight detonation, producing a white wreath of smoke (phosphoric acid), which gradually expands as it ascends.

The effect of the simultaneous action of phosphorus and an alkaline base upon water is the production of a hypophosphite, together with phosphuretted hydrogen (see § 114).

The spontaneously inflammable gas may also be obtained by acting upon phosphide of calcium with water.

When preserved for some time this gas loses its spontaneous inflammability, in consequence of the decomposition of the small quantity of liquid phosphide of hydrogen (as already described) to which it owes this property. Many substances which possess the property of decomposing the liquid phosphide (such as hydrochloric acid, or oil of turpentine) deprive the gas at once of its spontaneous inflammability, which may, however, be restored by acting upon the uninflammable gas with an oxidizing agent (such as binoxide of nitrogen), which, by abstracting a portion of hydrogen, reproduces a small quantity of the liquid compound, which remains diffused through the gas.

Phosphuretted hydrogen gas (when spontaneously inflammable) also takes fire in chlorine gas, burning with a greenish-white light, and yielding hydrochloric acid and pentachloride of phosphorus. Many metals extract the phosphorus from this gas at high temperatures, yielding metallic phosphides and free hydrogen. Some metallic solutions decompose phosphuretted hydrogen; with sulphate of copper a black precipitate is formed; the gas, however, is not entirely absorbed, but loses its inflammability.

The analogy of this compound, in some respects, to ammonia (to which it corresponds in composition) is remarkable. It unites with hydriodic acid, forming a crystalline compound analogous to chloride of ammonium, which is decomposed by water with evolution of phosphuretted hydrogen.

It also unites, like ammonia, with the higher oxides of tin, antimony, iron, and other metals, forming white saline compounds.

PHOSPHORUS AND CHLORINE.

§ 117. These two elements unite with considerable energy, producing two different compounds, the *terchloride* and *pentachloride of phosphorus*.

TERCHLORIDE OF PHOSPHORUS, PCl_3 . *Sp. Gr.* 1.45.

This chloride is formed by passing dry chlorine gas into or upon fused phosphorus, in a retort moderately heated in a sand-bath, until nearly the whole of the phosphorus is converted into terchloride, which distils over into a receiver.¹

It is a colorless transparent limpid liquid which has a pungent odor, resembling that of hydrochloric acid, and fumes when exposed to the air; it boils at $172^{\circ}.4$ F. (78° C.)

When mixed with water, it is gradually decomposed into hydrochloric and phosphorous acids:—



Terchloride of phosphorus dissolves a small quantity of phosphorus with the aid of heat, the solution depositing a film of phosphorus as the liquid evaporates.

¹ Since the amorphous phosphorus has been introduced into general use, the danger attending the preparation of both chlorides of phosphorus has been considerably diminished.

PENTACHLORIDE OF PHOSPHORUS, PCl_5 .

This compound is produced by allowing phosphorus to burn in excess of dry chlorine gas (which it does spontaneously at ordinary temperatures), or by acting upon the trichloride of phosphorus with chlorine, which gradually converts it into the solid pentachloride. The latter is a snow-white, flocculent substance, which volatilizes below 212°F .; its vapor density is 4.85 at 365°F . (185°C .); it may be fused under pressure, and crystallizes, upon cooling, in transparent prisms. It fumes on exposure to air, and is decomposed by water into phosphoric and hydrochloric acids:—



It forms, with metallic oxides, chloride of the metal and phosphate of the oxide. Pentachloride of phosphorus, like phosphoric acid, is sometimes employed as a dehydrating agent; it has also lately been used for producing chlorine compounds of organic derivation.¹

OXYCHLORIDE OF PHOSPHORUS, PCl_2O_5 . *Sp. Gr.* 1.7.

Pentachloride of phosphorus is gradually converted by aqueous vapor into hydrochloric acid and the above compound:—



This substance is always produced after a time, if pentachloride of phosphorus be preserved in an imperfectly-stoppered bottle.

It is a colorless liquid, very limpid, and of high refracting power. It boils at 230°F . (110°C .), yielding a vapor of the density 5.40; its odor is similar to that of trichloride of phosphorus. It fumes in air, and is decomposed, by contact with water, into hydrochloric and phosphoric acids.

CHLOROSULPHIDE OF PHOSPHORUS, PCl_2S_2 .

When dry hydrosulphuric acid is passed over pentachloride of phosphorus, or when the latter is agitated in a vessel filled with the dry gas, a colorless liquid of the above composition is obtained, which boils at 262°F . (128°C .); it is slowly decomposed by water into hydrochloric, hydrosulphuric, and phosphoric acids:—



It is converted into *sulphophosphoric acid* by alkalies, a metallic chloride being simultaneously produced:—



The sulphophosphates may be crystallized; they correspond to the tribasic phosphates, the formula of *sulphophosphate of soda* being—



This acid may be replaced in its combinations with bases by the weakest acids; when thus liberated, it is at once decomposed into hydrosulphuric and phosphoric acids:—



PHOSPHORUS AND BROMINE.

When phosphorus and bromine are brought into contact in a vessel filled with

¹ Compounds of pentachloride of phosphorus with various acids (*e. g.* sulphuric, phosphoric, arsenious, and tungstic acids) have been obtained.

² By the action of sulphur on pentachloride of phosphorus, Gladstone has obtained a liquid compound to which he ascribes the formula PS_4Cl_2 .

carbonic acid, they unite instantaneously, with incandescence, the products being a solid or a liquid, according to the proportions used.

Terbromide of Phosphorus (PBr_3) may be obtained by adding phosphorus, in very small pieces, to perfectly anhydrous bromine, until the color of the latter disappears perfectly; excess of phosphorus may be separated by distillation.

It is a colorless, very volatile, pungent liquid, which does not solidify at $10^{\circ}.4$ F. (-12° C.); when in contact with air it emits white fumes; and is decomposed by water, with considerable evolution of heat, into hydrobromic and phosphorous acids. It has also the property of dissolving phosphorus.

Pentabromide of Phosphorus (PBr_5) may be formed by mixing the terbromide with bromine, or by bringing a small excess of the latter in contact with phosphorus.

It is a lemon-yellow solid substance, which crystallizes in the rhomboidal form after fusion, and may be obtained in needles by sublimation. It evolves dense fumes in air, and is converted by water into hydrobromic and phosphoric acids.

An *oxybromide of phosphorus*, analogous to the oxychloride, of the formula PBr_3O_2 , also exists.

PHOSPHORUS AND IODINE.

These two substances unite with energy at ordinary temperatures, the phosphorus bursting into flame if air have access. The phosphorus appears to unite with iodine in several proportions; 1 of the former to 24 of the latter forms a black mass, fusing at $104^{\circ}.8$ F. (46° C.); 1 to 16 forms a dark gray crystalline substance, fusing at $84^{\circ}.2$ F. (29° C.); and 1 to 8 an orange-yellow mass, fusing at 212° F. (100° C.); all three are decomposed by water, yielding hydriodic acid; and in addition, the first yields phosphoric acid, the second phosphorous acid, and the third phosphorous acid and phosphorus.

PHOSPHORUS AND NITROGEN.

Ammoniacal gas is absorbed by both the chlorides of phosphorus.

The terchloride of phosphorus yields a white solid which is sparingly soluble in water, and has the composition $PCl_3.5NH_3$. When this compound is heated in a current of carbonic acid, it is resolved into hydrogen, ammonia, phosphorus, and *phosphide of nitrogen*, N_2P . This last is a white amorphous powder, insoluble in all menstrua; it is infusible and does not volatilize at a red heat if air be excluded, but is slowly oxidized when heated in air; when heated in hydrogen it yields ammonia. It is but slowly affected by powerful oxidizing agents.

Gerhardt states that this compound contains hydrogen, and assigns to it the formula PN_2H , with the name *phospham*.

When the pentachloride of phosphorus is saturated with ammoniacal gas, chloride of ammonium is produced, together with a white insoluble substance, of the formula $N_2P.2HO$, to which the names *phosphamide* and *hydrated phosphide of nitrogen* have been given. When boiled with water, especially in presence of acids and alkalis, it yields phosphoric acid and ammonia.

When heated out of contact with air, it evolves ammonia, and leaves a gray insoluble residue, which fuses, but is not decomposed when further heated; its formula, according to Gerhardt, is PNO_2 .

When the mass obtained by the action of moist ammonia upon pentachloride of phosphorus is distilled with water, a white substance passes over, which crystallizes in regular prisms; it fuses below 212° F., and may be distilled unchanged; it is insoluble in water and acids, but dissolves easily in alcohol and ether, and appears to possess great stability.

This body has been named the *chlorophosphide of nitrogen*; its formula is $N_2P_2Cl_2$.

PHOSPHORUS AND SULPHUR.—These elements combine in a number of different proportions; if phosphorus and sulphur be very gently heated together,

they unite with disengagement of much heat, and frequently with explosion. The safest method of causing them to combine is by fusing the phosphorus in a flask under water, and then introducing gradually, small fragments of sulphur. Compounds of a pale yellow color are thus produced, which have been shown by Berzelius to consist of a series of sulphides of phosphorus, analogous to the oxides of that element, as is seen by the following comparison:—

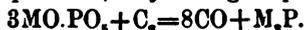
Subsulphide of phosphorus	P_2S	Suboxide of phosphorus	P_2O
Protosulphide	" PS	Hypophosphorous acid	PO
Tersulphide	" PS_3	Phosphorous acid	PO_2
Pentasulphide	" PS_5	Phosphoric acid	PO_5
Persulphide	" PS_{10}	<i>No analogous oxygen compound.</i>	

They are prepared by fusing together the two elements, in the proper proportions, in the manner described. They are insoluble in water, alcohol, and ether; of the first two there are red modifications. They combine with alkaline sulphides, and give rise to the production of sulphur-salts, analogous to the corresponding salts of the oxides of phosphorus.

PHOSPHORUS AND SELENIUM appear likewise to be miscible in all proportions, at a temperature approaching the fusing point of phosphorus.

No formulæ have yet been assigned to the selenides of phosphorus.

METALLIC PHOSPHIDES.—The affinity of phosphorus for metals is not so powerful as that of sulphur; nevertheless, it unites with the greater number, producing *phosphides*. These may be obtained by direct union of the metal and phosphorus at elevated temperatures, or by heating the phosphates with charcoal:—



They may also be formed by heating metallic oxides with phosphorus, or by bringing gaseous phosphuretted hydrogen in contact with salts of the metals. They are solid, opaque, and frequently possess metallic lustre. Many of them part with their phosphorus at high temperatures, the corresponding phosphates being sometimes produced at the same time, if air be allowed access. They are converted, by nitric and hypochlorous acids, into phosphates. The alkaline phosphides are decomposed by water, phosphuretted hydrogen being evolved, and hypophosphite of the metallic oxide produced.

CARBON.

Sym. C. Eq. 6. Sp. Gr., as diamond, 3.5 to 3.55 (as graphite, 1.9 to 2.3).

§ 118. Lavoisier was the first to show that carbonic acid consisted of oxygen and another element, *carbon*; and that this element existed in the pure state as the diamond. Carbon is also found, nearly pure, in plumbago, or graphite, and in anthracite. In coal it is associated with iron, hydrogen, earthy and alkaline compounds, &c. In most vegetable and animal substances it is the principal constituent; it also occurs in many minerals, in combination with oxygen (as carbonic acid).

The DIAMOND occurs principally at Golconda, in Borneo, and Brazil. It is found in gravel or sand, or in a kind of conglomerate of fragments of chalcedony, jasper, and quartz. Diamonds are generally found rough, and coated with a crust which renders them but slightly translucent; on removing this, however, they are very brilliant, and generally colorless and transparent, though they also occur black, yellowish or brown, blue, green, and rose-colored. They refract light powerfully. The regular octohedron is the primitive form of the diamond; its most general form, however, is that of the octohedron, of which the planes are replaced by low pyramids of three planes, so that the figure presents twenty-four planes, and is

therefore almost spherical in form. The surfaces of the crystal are seldom flat, having generally become curved, in consequence of the continued attrition to which they have been subjected in the motion of the alluvial materials with which it is associated; in fact, the action of this attrition is so considerable, as frequently to have reduced crystals of the form just described to that of an octohedron with convex faces.¹

The diamond is the hardest of all gems, its natural facets being harder than those produced by polishing. The glazier, in choosing the diamond for cutting glass, makes use of an edge of the crystal formed by naturally curved surfaces, since the edges formed by flat planes merely scratch the glass without producing any fissure.

The diamond may be cleaved in the direction of the octohedral plane; it can only be polished by means of its own dust. The diamond may be exposed to a white heat in a closed crucible without undergoing any change. When heated in air, it begins to burn at about the fusing-point of silver. If it be placed between the two charcoal points of a very powerful battery, it becomes so brilliant from incandescence that the eye is dazzled when looking at it; but if viewed through a smoked glass it will be observed to swell up considerably and divide into fragments. When cold, it is no longer transparent, but metallic gray in appearance, and very friable, resembling coke formed from bituminous coal. Fused nitre rapidly oxidizes the diamond, the carbonic acid produced being retained by the potassa in the nitre. Its examination according to this method affords the best proof of its being pure carbon.

GRAPHITE, BLACK-LEAD, OR PLUMBAGO, is another crystalline modification of carbon, very different in appearance and physical properties to the diamond. It is found imbedded, in the form of rounded masses, in strata of limestone, mica-schist, and granite. The most celebrated locality for this mineral is Borrowdale, in Cumberland. The crystalline form, in which it is occasionally found, is the six-sided table; it generally consists, however, of aggregates of small gray metallic scales, perfectly opaque, soft, and unctuous to the touch; it may be easily cut, and produces a lead-gray mark upon paper. It always contains an admixture of manganese and iron (existing apparently as oxides, combined with silicic and titanitic acids). Some specimens contain as much as 28 per cent. of these impurities, while in others only traces are found. Graphite, like the diamond, is unalterable by heat. It may be prepared artificially by bringing an excess of charcoal in contact with fused cast-iron; a portion of the carbon dissolves, and separates out again on cooling, in large scales.

§ 119. COAL.—The form in which carbon is found most abundantly in nature is that of coal, in which substance it is associated with other bodies, very variable in their nature.

Microscopic examination of the various kinds of coal leaves no doubt that they are of vegetable origin; even the most massive coals exhibit some evidence of vegetable structure, and in others of inferior order, the complete forms of various portions of plants are frequently found compressed between the layers, more or less perfectly transformed into coal. These observations, added to the results of careful researches on the subject, render it evident that coal has been produced by the combined action of heat and pressure upon vegetable matter; in short, that it consists of the vegetation of former ages, which has been buried beneath waters, and subsequently become gradually transformed into coal by the effect of heat, generated by the action of moisture, assisted by the pressure of deposits of mud, sand, or clay, which had gradually displaced the water. This process of subterraneous combustion appears, indeed, to have been analogous to that ob-

¹ Diamond in the amorphous state, of a brownish-black color, has been found in Brazil, and also in some parts of Switzerland.

served when vegetable matter, such as hay, flax, &c., is closely packed in a moist state, when it is found gradually to undergo a species of fermentation, or slow combustion, evolving inflammable vapors, and becoming ultimately carbonized.

All vegetable matter, if exposed in a moist state to very considerable pressure, the escape of the gaseous matter being thus, to a great extent, prevented, would become converted into bitumen, lignite, brown coal, or even perfect coal, according to the intensity and duration of the action. Gaseous compounds, rich in carbon, evolved by the first action of heat, would, under these circumstances, be robbed of a portion of that constituent as the temperature increased, or even suffer entire decomposition with deposition of carbon (see § 129).

In laying bare or removing deposits of coal, quantities of inflammable gas, known as fire-damp (carburetted hydrogen), are continually found pent up in fissures, or gradually escaping from the pores of the coal, in which it has remained for ages compressed. The inflammable gas frequently found escaping from morasses and stagnant pools, to which the name marsh-gas has been given, evidently results from the same species of fermentation, or partial combustion of vegetable matter inclosed under water in the slime and mud; the resulting gaseous products (carburetted hydrogen, carbonic acid, &c., making their escape to the surface of the water, since the pressure exerted upon them is insufficient to retain them. After a time, the mass covering the surface of the earth in such localities is found to consist of imperfectly-charred vegetable matter, to which the name *peat*, or *turf*, is given, and which evidently represents the coal in its first stage of formation.

Upon examining the different kinds of coal, they are found to vary considerably in composition and appearance, according to the temperature to which they have been exposed, and the period of their formation.

The more perfect the conversion of vegetable matter into mineral charcoal has been, the smaller is the proportion of elements (hydrogen and oxygen) found in the coal, which originally existed as, or are easily convertible into, volatile compounds.

The *brown-coal*, or *lignite*, represents the earliest stage of the process of carbonization, and is the coal of most recent formation. It has a brown, earthy, and sometimes fibrous and woody appearance; large masses of it are found retaining the original form of the trunks of trees, and others containing very perfect forms of leaves, &c. This coal contains from 57 to 70 per cent. of carbon, from 6 to 8 per cent. of hydrogen, and from 14 to 37 per cent. of oxygen, besides nitrogen, and earthy and alkaline salts. Some varieties (particularly *alum-shale*), contain a large quantity of alumina, and are employed extensively for the manufacture of alum.

The *black-coal*, or *pit-coal*, is in a far more advanced state of carbonization than the lignites, but still contains a considerable amount of bituminous matter.

Under this head are classed many varieties of coal. The most bituminous of these is the *cannel coal*; it is dense, black, devoid of lustre, exhibiting a conchoidal fracture, and capable of receiving a high polish. When held in the flame of a candle, it easily ignites, burning with a steady, bright flame. This coal has of late come into very extensive use for the manufacture of illuminating gas, of which it yields a better quality than other species of coal.¹ The other varieties of pit coal also possess a laminated structure, and more or less brilliancy; the principal kinds have received the names, *pitch-coal*, *cubical coal*, *splint coal*,

¹ A species of cannel-coal (the *hog-head coal*) found at Bathgate, in Scotland, has lately received extensive application. When submitted to distillation, it yields a large quantity of oily matter, which is very valuable as a lubricating agent, and from which a peculiar crystalline solid, termed paraffine, may be separated. This latter has been proposed as an illuminating material.

and *caking coal*. When exposed to heat, they soften (some swelling up considerably), burn with a bright flame, and leave but little ash. The caking coal is the most readily inflammable, burns the longest, and easily agglutinates when heated in large masses (whence its name). It is therefore employed for the manufacture of gas and coke, in preference to the other kinds of pit coal.

Pit coals contain from 74 to 89 per cent. of carbon: impressions of leaves and plants, or a fibrous woody structure, frequently appear in some of them; almost every species contains, in addition to the ordinary mineral constituents, iron-pyrites (bisulphide of iron), sometimes in layers of distinct crystals, and sometimes very finely disseminated. This is the most objectionable of all constituents met with in coal, as will be presently noticed.

The *glance-coal* or *anthracite* (*Welsh coal*) is the oldest of all kinds of fossil charcoal, and must be regarded as the last stage of carbonization; hence it differs very considerably, both in its composition and nature, from the other kinds of coal. It is homogeneous, and totally devoid of impressions of plants, has a massive structure, conchoidal fracture, a vitreous lustre, and frequently exhibits a powerful play of color (*e. g.* the so-called *peacock* coal). It contains from 90 to 95 per cent. of carbon. It is of all kinds of coal the most difficult of combustion,¹ and only burns with a flame in a powerful current of air.

Jet is also a species of coal of this class: it is bituminous, and sometimes goes by the name of pitch coal.

§ 120. *Decomposition of Coal*.—That the action of heat upon the organic portion of coal must vary considerably, according to circumstances, is obvious. When subjected to heat in confined spaces (*i. e.* destructive distillation), a great variety of products, more or less volatile and inflammable, escape, and a porous substance, consisting of carbon, together with the inorganic constituents of coal, remains behind, to which the name of *coke* is given. A detailed account of this decomposition will be found in the article on coal-gas (§ 126).

The most simple decomposition which coal undergoes, is its conversion by heat, and an unlimited supply of air or oxygen, into the ultimate products, carbonic acid and water, and a small quantity of ammonia; but even this result may be modified, if the whole mass of coal acted upon does not undergo simultaneous combustion; the carbonic acid becoming partially reduced to carbonic oxide as it comes into contact with that portion of the coal which is highly heated, but not supplied with the oxygen necessary for its combustion. (§ 123.)

The burning of coal, in an ordinary fire, for example, is, however, a process of far more complicated nature. The heat produced by the first burning portion (*i. e.* the outer surface), subjects the greater mass of coal to dry distillation, a variety of volatile products being thus formed, mostly of an inflammable nature, which therefore burst into flame as they come into contact with the burning coal and with oxygen. Some of these, being rich in carbon, burn with a bright flame, the results being water, carbonic acid, and a considerable amount of unconsumed carbon, which is carried off in a finely divided state, together with the products of combustion and other volatile matters which escape the action of heat and oxygen, thus producing what is called smoke, and depositing itself partially upon cool surfaces in the form of *soot*. If the combustion of the coal be not carried to the fullest extent, a porous *cinder*, similar to coke, will remain behind, which no longer contains any constituents volatilizable by the action of a bright red heat, but consists of carbon and the ash of the coal. This cinder will gradually glow away, if maintained at a sufficient temperature, until the inorganic constituents of coal alone remain in the form of an ash.

Inorganic Constituents of Coal.—The nature of the inorganic or mineral por-

¹ Anthracite is now extensively used as fuel, not only on a large scale (in smelting processes), but also on a small scale in metallurgic operations.

tion of the coal is greatly influenced by the species of rock near which the seam runs; it is found generally to contain, besides the ordinary mineral constituents of plants, those derived from portions of the rock which have been gradually carried into the pores of the coal. The mineral substances most generally found in greater or less abundance in different kinds of coal, are potassa, lime, magnesia, iron, manganese; silicic, phosphoric, and sulphuric acids; sulphur, chlorine, and sometimes traces of iodine. Of some of these it is difficult to say how they originally exist in coal, since, in obtaining the ash in which they are detected by burning the coal, their combinations amongst each other must undergo important modifications.

Iron exists, as already stated, chiefly as iron-pyrites (FeS_2), which, when heated, parts with one portion of its sulphur, becoming (proto-) sulphide of iron, the sulphur being converted into sulphurous and other acids.¹ The sulphide is partially oxidized, yielding sulphate of iron, and also sesquioxide of iron. The sulphur undergoes various degrees of oxidation; hyposulphurous and hypsulphuric acids, in combination with potassa or lime, are sometimes found in the ash of coal. Sulphate of lime exists in large quantities in some kinds of coal, and is always found in coal-ash. The potassa and a portion of the earths, as also iron and manganese, are found in the ash as carbonates. Some ashes contain likewise chloride of potassium.

Estimation of the Value of Fuel.—It is of the highest importance that we should be enabled to arrive at an accurate idea of the value of different kinds of coal or fuel in general, with reference to their heating qualities; in other words, with regard to the amount or intensity of heat produced by their perfect combustion in air. The means presented for this purpose by what are called *pyrometers*, furnish by no means results to be depended upon; the most simple method is, therefore, to determine the *relative* heating powers of different fuel. This may be easily effected by ascertaining the amount of water raised from the temperature of 32°F. (0°C.) to 212°F. (100°C.), by combustion of a standard weight of the different kinds of fuel: thus, it has been found that

Part by Weight.		Water raised from 32° to 212° .
1	pure carbon . . .	78 parts by weight.
1	wood charcoal . . .	75 “
1	dry wood	36 “
1	good coal	60 “

It is obvious that in this way the relative value of different kinds of fuels may easily be measured and calculated.

Another method of determining the heating power, is to ascertain the amount of oxygen necessary for the combustion of a certain amount of coal. This is effected by mixing the finely divided fuel with a substance containing oxygen, which is not expelled by mere application of heat, but is very easily abstracted by substances having an affinity for it at an elevated temperature. The method adopted is to mix the pounded and dried coal with pure litharge (PbO), and to maintain the mixture in a state of fusion for some time in a Hessian crucible, which, when the mass has subsequently become cool, is broken, and the lead, reduced from the oxide by the action of the carbon and hydrogen, is found at the bottom; from the quantity of lead reduced, the amount of oxygen consumed in the combustion or oxidation of the coal is easily calculated.²

¹ The presence of iron-pyrites in coal is exceedingly injurious to furnaces, or any metal work with which the hot coal comes in contact, since it easily parts with a portion of its sulphur, thus acting rapidly upon the metal. Coke prepared from coal containing much pyrites, acts injuriously in the same manner.

² The estimation of the value of coal, however, is not complete without some experiments upon its mechanical nature. To ascertain, for example, what quantity of coal

The *carbon* and *hydrogen* (which are the two heating constituents in coal) may also be separately determined from the amount of carbonic acid and water produced by the complete oxidation of a known weight of coal; this is effected by burning the powdered coal with oxide of copper (the action of which is sometimes aided by the addition of free oxygen), and collecting the products in the manner usually adopted in organic analysis.

The *nitrogen* in coal, which varies in amount from 1 to 2 per cent. may be determined according to the method of Will and Varrentrapp.

Determination of the Sulphur.—About 20 grains of finely-powdered coal are mixed with an equal weight of pure carbonate of soda; the resulting powder is then well mixed with one part of pure nitrate of potassa, and four parts of pure chloride of sodium; the mixture is introduced into a platinum crucible (which should not be more than half-filled), and maintained in a state of gentle fusion until the whole of the carbon has been oxidized by the nitre, and the mass appears white. The crucible is then allowed to cool, and afterwards immersed in a beaker containing distilled water, acidified with hydrochloric acid, whereby the fused mass is dissolved, and the carbonic acid liberated. The sulphuric acid now in solution, which has been produced by the oxidation of the sulphur by the nitre, may be determined by precipitation as sulphate of baryta (*see* Quantitative Analysis). From the amount of sulphuric acid formed, the percentage of sulphur present in the coal is easily calculated.

The following is also a very neat method of determining the sulphur: A weighed quantity of dried coal is mixed with twice its weight of carbonate of magnesia, and the mixture placed in a tube of Bohemian glass, which is then strongly heated while a slow current of oxygen is allowed to pass over the mixture. The organic matter is soon oxidized, and the sulphur converted into sulphuric acid, which unites with the magnesia, expelling the carbonic acid. As soon as the heated mass has become quite white, the tube is allowed to cool, broken up, and digested in warm water; the sulphate of magnesia is thus extracted from the mass, and the amount of sulphur determined in the aqueous solution, as directed above.

Of the agents employed in the first of the above methods, the most important member is the nitre, which oxidizes the carbon, hydrogen, and sulphur in the coal; if used alone, however, its action on the coal would be very intense, and much loss would ensue in consequence of the violent effervescence of the liquid mass; this action is moderated by the addition of the chloride of sodium, which being a substance of no active properties, and at the same time tolerably fusible, serves as a capital diluent.

Estimation of Ash.—From 10 to 20 grains of the finely-pulverized coal are dried perfectly by exposure in the air-bath to a temperature of 248° F. (120° C.), and then carefully ignited in a platinum crucible over a gas-flame, or that of a roaring-lamp, until the whole of the combustible matter is consumed. The crucible, being supported by a wire triangle, is placed in a slanting position, the mouth is closed by loosely placing the lid upon it, until no more volatile matter is observed to escape, when the orifice is partly opened, in order to allow of the entrance of air into the crucible. The ash should be stirred about, from time to time, by means of a piece of thin platinum wire, so as to expose a fresh surface to the action of the air that enters the crucible. When the whole of the organic matter appears to be burnt off, the crucible is allowed to cool, and weighed, after which it is once more strongly ignited, and reweighed; this is repeated until the

would be likely to be disintegrated by carriage; how much coal could be stowed away in a certain space, &c. &c.

Certain *patent fuels*, presenting considerable advantages as far as facility of stowage is concerned, have been lately manufactured, by mixing coal-dust and waste with bituminous matters, and moulding the resulting mass into bricks.

numbers from two consecutive weighings are alike. It is found very difficult, in many instances, to burn off the last traces of carbon from the ash of coal, particularly if it be a caking coal; in such cases, it is necessary to resort to an auxiliary agent, in order to obtain a perfectly pure ash.

One method is, to cover the crucible containing the ash, with a lid having a perforation in the centre, through which a tube of porcelain, or of platinum, may be allowed to enter the crucible. By means of this tube, which is connected with a gas-holder containing oxygen, a very moderate current of that gas may be allowed to enter the crucible, and by coming in contact with the ash at a low red heat, to oxidize rapidly the last traces of carbon. The surface of the ash in the crucible must be changed, from time to time, in the manner directed.

A perfect oxidation of the carbon may also be effected by mixing the ash, after it is burnt as thoroughly as possible with a small quantity of pure oxide of mercury, and then applying a moderate heat, when the carbon will be rapidly oxidized at the expense of the oxygen in the oxide, the mercury being at the same time volatilized. This operation is conducted in an open crucible or capsule.

Estimation of Coke.—About 100 grains of the dried coal are exposed, in a covered porcelain crucible, inclosed in a Hessian crucible, to a bright red heat for about an hour.

The proximate analysis of coal—i. e. the determination of the products of its destructive distillation, may be executed in the following manner (*Bunsen and Vieillard*):—

A weighed quantity of coal is heated in a tube of hard glass, and the coke remaining after the operation is weighed in the tube.

The products of the distillation are collected in the following apparatus:—

1. A cooled receiver for condensing the tar, water, and ammonia.
 2. A tube filled with chloride of calcium, to retain any water and ammonia which may have escaped.
 3. A bulb apparatus containing a solution of oxide of lead in potassa, to retain sulphureted hydrogen and carbonic acid.
 4. A drying tube with chloride of calcium.
 5. A bulb apparatus containing perchloride of arsenic, to absorb olefiant gas and vapors of hydrocarbons.
 6. A bulb apparatus containing an alcoholic solution of potassa, to absorb any volatile alkaline products.
 7. A bulb apparatus containing sulphuric acid.
 8. A graduated scale tube to measure the condensed gases.
- The gas which has not been retained by the substances in which it is condensed is kept for a few minutes in a gas-holder, the principal of which are carbonic oxide, carbonic acid, hydrogen, and cyanogen.
- It is then a measure of the gradual absorption of carbon from coal-gas at a high temperature upon the introduction of the gas-holder which is frequently used as a convenient method of testing the strength and masses, of a small boiler, and measuring the extent of its structure, somewhat resembling pyrolysis. It is used for the purpose of determining the amount of carbon from the high temperature resulting from its combustion, and also for purposes of the small boiler, which is a useful method of testing the strength of coal, from which it is known, according to various methods. The most method of preparing the boiler is being to use a large boiler without extending the boiler to the boiler, which is made somewhat is prevented by a series of high and low boiler. Sometimes boilers are constructed with a series of high and low boiler, which is made off the boiler time to time to the boiler, which is made off the boiler by a series of high and low boiler. The highest pieces of coal

are placed at the base of the mound, and care is taken in constructing the latter, to have free channels leading from the apertures in the chimney to the circumference. The outer surface of the mound is covered with a coating of cinders. The ignition is effected by the chimney, into which burning coals are thrown, which communicate their flames to the mound through the apertures. Air is allowed to pass into the mound through spaces at the foot, and escapes through the chimney. As soon as the whole mass becomes redhot, the mouth of the chimney and the other apertures are closed, and the coke allowed to cool.

Coke is also very frequently prepared in furnaces of brick, provided with doors or slides, by which the access of air may be regulated. These furnaces are kept in operation day and night, receiving fresh charges of coal directly one charge of coke is withdrawn, while the furnace is still redhot, whereby the fresh charge of coal is ignited.

In the processes above mentioned, the secondary products of the coking, such as tar and gaseous matter, are not taken into consideration. Coke is, however, obtained in large quantities, as a secondary product, in the manufacture of gas, where the coal is submitted to destructive distillation in closed iron retorts. Good coke should be compact and in large pieces, not liable to crumble away. It yields upon incineration about 2 or 3 per cent. of earthy ash, and has a specific gravity varying from 1.6 to 2.

Wood Charcoal.—The temperature resulting from the combustion of charcoal is much higher than that from burning wood, in consequence of the absence of the large quantity of water which wood contains, amounting to between 50 and 60 per cent. The object of charring wood is therefore the removal of moisture, and, what is also of great importance, the concentration of the heating power of the wood to a smaller space, and the expulsion of those matters contained in it which become volatile before they are burned, thus rendering a large amount of heat latent.

Charcoal is prepared either by allowing the volatile constituents of the wood alone to undergo combustion, or by heating the wood in closed vessels, when, the air being excluded, all matters volatile at a high temperature, are expelled without undergoing combustion.

Charcoal is obtained, according to the first plan, in a similar manner to coke, by constructing heaps or mounds of wood, inclosed in a coating of charcoal-powder or sand, and supplied with fissures for the admission of air into the mass, which may be closed at pleasure, as the charring proceeds. The second method is that of charring the wood in furnaces or retorts, the volatile products being conducted into condensing apparatus, and thus preserved. In this manner, acetic or pyroligneous acid, wood naphtha, or pyroligneous ether, and tar, are obtained as secondary products.

The method and precautions adopted in charring wood, as also the choice of wood, depend much upon the use to which the charcoal is to be applied. If wood is heated in confined spaces beyond a certain period, it is found that the amount of combustible matter in a given volume no longer increases, but suffers an absolute loss; or, that when charcoal containing the maximum amount of combustible matter is required, the wood is only incompletely charred; in this state it is called *red charcoal* (*charbon roux*), and in economical respects possesses great advantages over the black charcoal obtained by the complete charring of wood; which being, however, more dense and compact than the latter, possesses the advantages of greater conducting power.¹ Wood which has been previously dried, yields a greater quantity of charcoal than the corresponding amount of damp

¹ For further particulars respecting the comparative value of *charbon roux* and black charcoal, see article on Gunpowder.

wood, as, in the latter case, carburetted hydrogen, and carbonic oxide are evolved when the wood is charred.

The most perfect charcoal is that which is prepared for the manufacture of gunpowder, for which purpose only certain kinds of wood are employed: viz. the alder, dogwood, poplar, maple, and walnut. The wood is charred in iron cylindrical retorts, which admit of the most accurate regulation of heat throughout the operation. They are sometimes connected with condensing apparatus for the reception of the volatile products, and are supplied with tubes in which pieces of test-wood are placed, and examined from time to time to ascertain accurately the period of requisite carbonization.

Frequently, instead of charging the retorts directly with the wood to be charred, it is packed into sheet-iron cylindrical cases (*slips*) provided with lids, and of such dimensions as to fit easily into the retort. A great saving of time and heat is effected by their use, as, when the wood has been properly charred, the case or slip containing it may be easily withdrawn, and another containing a fresh charge of wood at once introduced into the retort, without allowing the latter to cool down, as would otherwise be necessary.

When the charcoal is withdrawn from the retort, it is at once transferred into iron cases, provided with closely fitting covers, and is there allowed to remain until it has cooled down sufficiently to prevent its smouldering when exposed to the air. These cases are called the *extinguishers*.

The bark, small branches, leaves, and knots afford a dense hard charcoal difficult of combustion, chiefly on account of the greater amount of ash (silicates) which they contain, and which agglutinates at a high temperature. In preparing powder-charcoal, these portions are carefully removed before the wood is introduced into the retort, and the resulting charcoal is again looked over, as portions of this dense coal are frequently formed by the trickling down of drops of tar, which have condensed on the upper surface of the retort, upon the hot charcoal.

The *charbon roux*, already referred to, or, in other words, the charcoal containing the maximum amount of inflammable matter, is produced at a comparatively low temperature (about 540° F.); this has led to the proposal of a method (which has been carried out successfully), for preparing charcoal of this kind by means of heated steam of a certain pressure. The plan adopted consists in conducting steam from a boiler into a serpentine iron pipe, in which its temperature and tension are raised to the proper point by external application of heat; the heated steam is then allowed to pass into a copper cylinder inclosing a second, in which the wood to be charred is packed. The steam passing round the latter cylinder, heats the wood to such an extent as to liberate the tar and volatile matters; it is then allowed to enter the inner cylinder, when it thoroughly penetrates into the pores of the wood, expelling the volatile substances, which it carries with it as it escapes from another portion of the cylinder. The charcoal thus obtained is of a red-brown color, and is the kind generally used in France (where this method was worked out) for the manufacture of gunpowder.

The temperature to which the steam is heated in the serpentine tube, is ascertained and regulated by introducing into a large copper tube closed at one end (and reaching from the exterior of the outer cylinder into the inner one), small cylinders of tin, lead, or an alloy which will fuse at a certain temperature; upon these rest long thin iron rods surmounted by weights, which cause the rods to sink into the metal as soon as it softens or melts. By fixing into the cylinder several of these tubes containing alloys of different fusing-points, a proper range of temperature is obtained.

Thoroughly burned charcoal is brownish or bluish-black, presenting, when powdered, a smooth, velvet-like appearance. Its specific gravity varies exceedingly, according to its porosity.

Charcoal possesses the remarkable property of absorbing and condensing within

its pores, many times its volume of different kinds of gases, more particularly those liquefiable; thus it absorbs, of ammoniacal gas, 90 times its volume; of hydrosulphuric acid, 35; of oxygen, 9.25 its volume; of nitrogen 7.5, and of hydrogen 1.75 volumes. It likewise absorbs moisture from the air, and condensable vapors and effluvia of all descriptions (coke possesses the same property, though in a less degree). Freshly calcined charcoal also considerably retards the putrefaction of organic matter, if placed in contact with it. The interior of wine and of water casks is frequently charred before the introduction of the liquids; the wine being found to be improved in quality, and water to remain sweet, when thus placed in contact with charcoal. Spirits may also be easily deprived of the empyreumatic oil they frequently contain, by passing them through coarsely pounded charcoal. A property also possessed by charcoal, of absorbing various coloring matters, will be more particularly noticed, when we treat of animal charcoal. When vapor of water is passed over charcoal at a red heat, it is decomposed, a mixture of hydrogen, carbonic oxide, carbonic acid, and light carburetted hydrogen being produced.

Lampblack is the carbon deposited from combustible substances imperfectly burnt; such as tar, resins, oils, or gas. It may be obtained in the purest form by passing the vapor of alcohol or a volatile oil through a porcelain tube, heated to redness. On a large scale, lampblack is prepared by burning a resinous matter in large chambers with imperfect access of air; the product is collected on cloths hung round the chamber. A charcoal of the same description, though containing traces of hydrogen and oxygen, is obtained by igniting, in close vessels, sugar, starch, and substances of a similar nature.

Bone-black, ivory-black, or animal charcoal, is the charcoal obtained by calcining bones in close vessels. This charcoal contains about ten times its own weight of bone-earth in admixture, whereby it is distributed over a considerable surface. It possesses the property, to a high degree (common also to wood-charcoal to a less extent), of absorbing organic coloring matters; the charcoal obtained by calcining dried blood, hoofs, and horns, and hide-clippings, with carbonate of potassa, and afterwards extracting the calcined mass with water, possesses this property in the highest degree. It is very remarkable that this property of charcoal, though merely a mechanical attraction of surface, frequently overcomes chemical affinities of considerable intensity. Most organic bitter principles, as also organic bases,¹ when in combination with acids, are withdrawn from solutions by animal charcoal. The substances thus removed remain evidently upon the surface of the charcoal; the indigo is withdrawn from a neutral solution of that substance in sulphuric acid, upon its being passed through animal charcoal; the latter, however, again yields up the coloring matter when treated with solution of potassa. Animal charcoal has also the property of removing certain inorganic substances from their solutions; such as soluble subsalts of lead; iodine from its solution in iodide of potassium; lime and hydrosulphuric acid from their solutions; and metallic oxides from their solutions in caustic alkalies; several of the former being speedily reduced to the metallic state, apparently by the action of carbon in the very close state of proximity into which they are brought with it. Neutral salts are not affected to any extent by animal charcoal. If the animal charcoal is deprived of the bone-earth it contains, by treatment with an acid, its decolorizing and abstracting properties are considerably diminished, probably in consequence of its being rendered more compact. When animal charcoal is heated in chlorine water, it gradually disappears, being converted into carbonic acid.

§ 122. *General Properties of Carbon*.—Carbon is a dimorphous substance (crystallizing in two different forms, as graphite and diamond); it is a bad con-

¹ This property was recently applied by Graham and Hofmann in the examination of bitter ales for strychnine.

ductor of heat, and ordinary wood-charcoal is also a bad conductor of electricity; but when calcined at a high temperature, it becomes, like graphite, a very good electric conductor. When submitted to the action of a very powerful battery, carbon becomes softer by the intense heat; it then slightly vaporizes.¹ Upon exposure to a temperature of this description, all kinds of carbon are converted into a soft, friable coke, similar to graphite. Though carbon, in the various modifications in which it occurs, is possessed of very different properties, its general chemical character is, under all circumstances, the same.

The only instance of the artificial crystallization of carbon which we possess, is the manner in which it separates from its solution in fused iron, as already noticed. Carbon is not possessed of active chemical properties at low temperatures; it is remarkable for its non-volatility and insolubility; it cannot be dissolved unless oxidized, as by nitric or sulphuric acid, or chlorine water. The hypothetical density of carbon vapor, calculated from the densities of carbonic oxide and carbonic acid, is 0.414. Carbon burns readily in air or oxygen, when raised to a certain temperature (varying with the density of the different varieties), the product being carbonic acid, a colorless gas. When burnt in a limited supply of air or oxygen, carbon is converted into carbonic oxide, which consists of equal equivalents of carbon and oxygen. Carbon also combines with chlorine, phosphorus, and sulphur, and unites with some of the metals at high temperatures, producing metallic *carbides* or *carburets*.

The powerfully deoxidizing action of carbon, even at ordinary temperatures, has recently been demonstrated in a striking manner by Schönbein. He succeeded in reducing solutions of several salts of the sesquioxide of iron to the corresponding salts of the oxide, by simple agitation of their solutions with charcoal powder. By the same method, chloride of mercury was reduced to subchloride, and the nitrate of oxide to that of the suboxide.

Uses of Carbon.—This element, in its various forms, meets with a most extensive application in the arts and manufactures. Its powerful affinity for oxygen at a high temperature, and the further advantages which it presents in being infusible at the highest furnace-heat, and in forming gaseous products of combustion, render it the most suitable substance for effecting the reduction of metallic oxides.² The various modifications of carbon also meet with many special applications. The diamond is not only highly valued as the most precious of gems, but on account of its hardness is used for cutting and engraving glass, and in the state of dust for polishing hard metals and gems. Graphite is of the highest importance in the arts, being used for the manufacture of black lead-pencils. A more impure kind is also extensively employed for imparting a polished surface to iron, and protecting it from the action of air and moisture. Graphite, as well as highly calcined charcoal or coke, is used for surrounding the extremities of lightning-conductors, to facilitate the passage of electricity to the earth, in consequence of the good conducting powers of these forms of carbon. Coke and charcoal have long since become indispensable as fuel; the choice of either will depend upon the heat required, or other circumstances; the advantages they possess, in many respects, over wood and coal, have already been stated. Coke is also used for constructing the carbon cylinders of Bunsen's *Carbon-zinc Galvanic Batteries*. Powdered coal is coked in an iron mould of the proper form, and a great degree of compactness is afterwards given to the porous

¹ Desprez has succeeded in volatilizing and subliming carbon, by means of a Bunsen's battery of four hundred and ninety six cells.

² The indestructibility of charcoal under the influence of air and moisture receives many useful applications: thus it is customary to char the ends of stakes, piles, &c., before fixing them in the ground. Masses of charcoal were formerly buried as enduring landmarks.

cylinder thus obtained, by soaking it in a syrup and calcining it a second time. Charcoal points for the poles of batteries may be made in a similar manner.

The most important use of charcoal is its application in the manufacture of gunpowder: it is also used, in the freshly calcined state, as a deodorizer and disinfectant, in consequence of its power of absorbing effluvial vapor; the purification of water by charcoal filters is an example of this.

Lampblack is frequently of great use to the chemist, since it presents to him very finely-divided carbon in a tolerably pure state. It is also used extensively by colormen, and in the manufacture of blacking.

The decolorizing properties of animal charcoal, or bone-black, render it of considerable importance in manufactures; for example, in sugar-refining, in the manufacture of tartaric acid, &c.

The liquids to be decolorized are generally filtered hot through beds of coarsely-grained animal-charcoal, two or three feet in thickness. Several substitutes for bone-black, in which its composition is imitated, are employed successfully. Thus, 100 parts of pipeclay, made up into a thin paste with water, and thoroughly mixed with 500 parts of finely-powdered coal and 20 parts of tar, afford, when dried and calcined, a mass which is not much inferior in its decolorizing properties to bone-black. The recalcination of bone-black once used has been found considerably to diminish the decolorizing power, which arises from the deposition of a dense coating of charcoal upon its surface, produced by the decomposition of the organic coloring-matter absorbed. By allowing the sugar-filters to ferment, whereby the coloring matter is decomposed; the charcoal will, after being washed and recalcined, recover its power to a very great extent.

Since animal charcoal contains several inorganic constituents (phosphate and carbonate of lime, &c.), it is necessary to purify it before employing it for chemical purposes. This is effected by boiling it two or three times with hydrochloric acid in excess, until the acid solution is no longer precipitated by ammonia, and subsequently washing with water until all acid is removed. Its decolorizing properties are, however, greatly weakened by this purification.

The property which animal charcoal has of abstracting the salts of organic bases from their solutions, renders it also available as an antidote to vegetable poisons.

CARBON AND OXYGEN.

Carbonic oxide CO.
Carbonic acid CO₂.¹

CARBONIC OXIDE.

CO. *Eq.* 14. *Sp. Gr.* 0.967.

Composition by Volume.—2 volumes of carbon-vapor and 1 volume of oxygen form 2 volumes carbonic oxide.

§ 123. This gas is produced when carbonic acid is passed over charcoal, or some metals, at a high temperature; also when vapor of water is passed over well-burnt charcoal at a red heat, in an iron or porcelain tube; or by igniting chalk, or other carbonates, with the proper proportion of charcoal, or easily oxidizable metals.

Carbonic oxide is produced by the combustion of fuel in almost every furnace or fire. The first result of the action of the air upon the fuel at a high temperature is the production of carbonic acid gas; but as it passes upwards through the re-

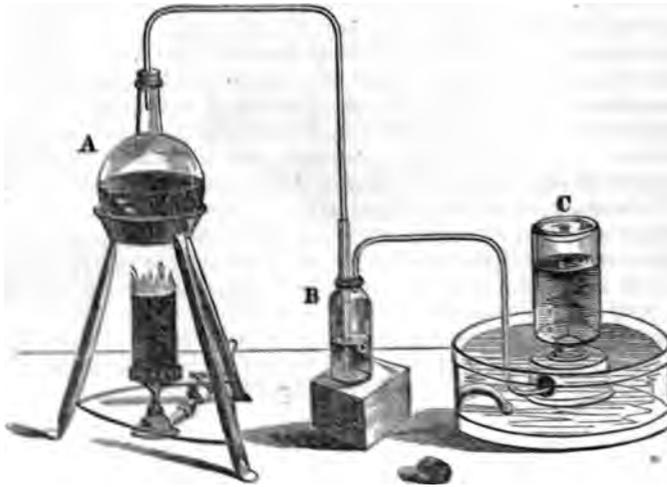
¹ Oxalic acid (C₂O₃), which is sometimes classed with the oxides of carbon, is not enumerated in this list, since it is not known to exist in the separate (anhydrous) state.

maining fuel, which is highly heated, but does not come in contact with air, the carbonic acid is reduced to carbonic oxide, a portion of the fuel being likewise converted into this gas by the other equivalent of oxygen. The gas thus produced is inflamed as it comes in contact with the air at the upper part of the fire, and is thus reconverted into carbonic acid.

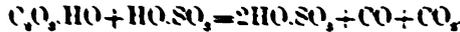
Carbonic oxide is likewise produced by the dry distillation of many organic substances, and by the decomposition of oxalic acid, or ferrocyanide of potassium, by concentrated sulphuric acid.

Preparation.—The two last-named substances are most generally employed for the production of carbonic oxide. Oxalic acid consists of two equivalents of carbon and three of oxygen (or of two groups, CO and CO₂), combined with one equivalent of water. When heated with strong sulphuric acid, the latter seizes the water

Fig. 66.

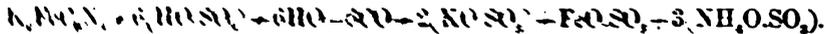


of hydration, which appears essential to the existence of oxalic acid, for, on its abstraction, the latter is immediately resolved into equal volumes of carbonic acid and carbonic oxide:—



The resulting mixture of gases is passed through milk of lime, or through solution of potassa, which retain the carbonic acid.

When ferrocyanide of potassium is heated with 5 or 10 times its weight of concentrated sulphuric acid, it yields a large quantity of carbonic oxide, being decomposed, together with the water, by the action of the acid, according to the following equation:—



Properties.—Carbonic oxide is a colorless, odorless gas which has not yet been liquefied, and burns when in contact with air, with a blue flame, being thereby converted into carbonic acid. It does not support combustion or respiration; it is, indeed, highly poisonous, producing coma almost immediately, when inhaled pure.

According to Lavoisier, one part of carbonic oxide diffused through the air

(the absorption of carbonic oxide by the system of a large temperature is turned to advantage, upon a numerous scale, in the reduction of some metals, particularly iron, from their ores.

is sufficient to render it irrespirable (*see* § 124). Carbonic oxide has no action on vegetable colors; it is a neutral body, similar to water; it does not, however, combine either with acids or bases, like that substance. It is but slightly soluble in water.

Carbonic oxide, when mixed with an equal volume of dry chlorine, and exposed to the action of the sun's rays, unites with that element, producing

CHLOROXICARBONIC ACID, CHLOROCARBONIC ACID, or PHOSGENE GAS, which has the formula COCl_2 .

It is colorless, and possesses a peculiar sweet but suffocating odor. It is also produced without the influence of solar radiation, when carbonic oxide is passed through pentachloride of antimony, the latter being thereby reduced to the trichloride. Its production in this manner affords a ready means of testing for carbonic oxide, since the smallest quantity of phosgene gas produced is easily recognizable by its peculiar odor. Water decomposes this gas, producing carbonic and hydrochloric acids:—



Carbonic oxide is decomposed by potassium and sodium at a high temperature.

These metals, however, absorb a quantity of the gas at a lower temperature, hence they are employed to separate it from mixtures of hydrogen and carbon-hydrogen with carbonic oxide. In the preparation of potassium, where that metal and carbonic oxide are the chief products, there are produced small quantities of peculiar compounds of carbonic oxide, which, when heated with water, yield two acids, to which the names *croconic* and *rhodizonic acids* have been given. These, and other compounds, in which the existence of carbonic oxide as a radical is assumed, form a class termed the carbonic oxide series, of which the following are the members:—

(Carbonic oxide CO_2 .)

Carbonic acid	$\text{CO} + \text{O}$
Chlorocarbonic acid	$\text{CO} + \text{Cl}$
Oxalic acid	$2\text{CO} + \text{O}$
Oxamide	$2\text{CO} + \text{NH}_3$
Carbonoxide of potassium	$7\text{CO} + \text{K}_3$
Rhodizonic acid	$7\text{CO} + 3\text{HO}$
Croconic acid	$5\text{CO} + \text{H}$
Mellitic acid	$4\text{CO} + \text{H}$

CARBONIC ACID.

CO_2 . *Eq. 22. Sp. Gr. 1.529.*

Composition by Volume.—Two volumes of carbon-vapor, and two volumes of oxygen condensed to two volumes.

§ 124. Carbonic acid occurs in the atmosphere (as a product of combustion, respiration, and decay of various kinds); in considerable quantities in the mineral kingdom, combined with metallic oxides; also in all spring and river water, either in combination with earthy and alkaline bases, or dissolved in the water in an uncombined state. Carbonic acid issues from the ground in various localities (*e.g.* in Brohl, the Grotto del Cane, and in Pymont). It forms the deadly *chokedamp* of coal-mines.

Carbonic acid is produced by the combustion of all carbonaceous substances in oxygen or in air, or by submitting them to the action of oxidizing agents at a more or less elevated temperature.

It is also a product of respiration, fermentation, and putrefaction; and is formed when carbonic oxide is burnt in air, or mixed with half its volume of oxygen, and inflamed or ignited by the electric spark or prepared platinum.

Preparation.—Carbonic acid gas is obtained by the action of a mineral acid upon a carbonate; and is most readily procured by pouring moderately concentrated hydrochloric acid upon fragments of marble in a gas-generating apparatus. The carbonate of lime is thus converted into chloride of calcium, carbonic acid escaping with effervescence:—



It may also be prepared by acting upon chalk with dilute sulphuric acid.¹ Hydrochloric acid is, however, much to be preferred, since the sulphate of lime, which, in the above instance, is the resulting product, is very insoluble in water, and even more so in the presence of free sulphuric acid, and being therefore deposited upon the chalk or marble, prevents further action of the acid. Chloride of calcium, on the contrary, is exceedingly soluble. Carbonic acid may be collected over cold water, but cannot be retained over it for any length of time without some loss, on account of its solubility. Being considerably heavier than air, it may be easily collected by downward displacement.

When pure gas is required, it should be first allowed to pass through a small quantity of water, to retain any hydrochloric acid vapor that may be carried over mechanically, and afterwards through a drying tube filled with chloride of calcium.

Properties.—Carbonic acid may exist in the solid, liquid, and gaseous states. It is liquefied by pressure of 30 atmospheres at a temperature of 32° F., the amount of pressure required to liquefy it decreasing with the temperature.

Liquid carbonic acid may be obtained on a small scale by generating the gas in a Faraday's condensing-tube, by the action of sulphuric acid on carbonate of ammonia, the tube being kept at a very low temperature; it is prepared in larger quantities, according to the method described, § 37.

Liquid carbonic acid is colorless, and very mobile, possessing an elastic force of 38.5 atmospheres at 32° F. Its specific gravity at that temperature is 0.83; it is possessed of remarkable dilating power. Liquid carbonic acid is insoluble in water and fatty oils, but is miscible in all proportions with alcohol, ether, bisulphide of carbon, naphtha, or oil of turpentine; it is solidified at about -94° F. (-70° C.), forming a perfectly transparent, vitreous mass. If allowed to escape into air, liquid carbonic acid evaporates with great rapidity, one portion passing over into the gaseous state immediately, whereby the other portion is cooled down to so low a temperature as to become frozen.

Solid carbonic acid is most readily obtained according to Thilorier's or Natterer's method (§ 37); it then presents the appearance of snow, and is compressible like that substance. It is a bad conductor of heat; hence, although its temperature is probably as low as -148° F. (-100° C.), it may be handled without injury; if pressed upon the skin, however, it produces a blister similar to that caused by a burn. It may be preserved for some hours in the air in large masses, if surrounded by any non-conducting substance. When mixed with ether, it forms a soft, semi-fluid mass, which evaporates rapidly, producing the most intense cold, whereby mercury may be frozen in large quantities; a still more intense cold may be obtained by placing a mixture of the above description under the receiver of an air-pump, and rapidly exhausting the air and gaseous carbonic acid. When obtained by exposing liquid carbonic acid to a low temperature, the solid carbonic acid resembles ice; it appears to melt at about -97°.6 F. (-72° C.)

Gaseous carbonic acid is colorless; it possesses a slightly pungent, acidulous odor, is incombustible, and does not support the combustion of most substances. It imparts to tincture of litmus a peculiar wine-red color, differing considerably

¹ This method is always preferred when the carbonic acid is required for making aerated waters, since the hydrochloric acid is liable to be carried off in vapor, which condenses in the water.

from the onion-skin red produced by sulphuric acid; the blue color is, however, restored by exposure of the liquid to air, as the carbonic acid evaporates. At the ordinary temperature, water dissolves about an equal volume of carbonic acid; but this solubility is considerably increased by the application of pressure. It has been shown, however, that a volume of water always dissolves the same volume of carbonic acid under all pressures, and that the greater amount absorbed is dependent upon the condensation of the gas. Upon the removal of the pressure, the extra amount of gas absorbed escapes.

Solution of carbonic acid has an agreeably acid taste; it exerts a slight solvent action upon several salts, otherwise insoluble in water (*e. g.* carbonate and phosphate of lime). It is probable that the phosphate of lime contained in plants is supplied to them through the medium of the water percolating through the soils, since water is always more or less charged with carbonic acid absorbed from the atmosphere or other sources.

The great density of carbonic acid admits of its being poured from one vessel to another, like a liquid, provided the surrounding air be not agitated.

When inhaled pure, or even mixed with a considerable amount of air, carbonic acid produces asphyxia and death; acting as a narcotic poison.¹ It is frequently believed that such mixtures of air and carbonic acid as will allow a candle to burn, may be breathed safely by man or animals; hence the practice of lowering a candle into pits, wells, or other places supposed to contain vitiated air. It is, however, found that mixtures in which a candle may burn, will, if inhaled, produce, if not immediate insensibility, ultimately the most dangerous consequences. It is now generally allowed that the accidents resulting from charcoal fires in close apartments, are due rather to the carbonic oxide evolved by the incomplete combustion, than to the carbonic acid; the latter is not generally produced in sufficient quantity to cause death.

Carbonic acid may be shown to be a product of respiration, by breathing through a tube into lime or baryta water, which are almost immediately rendered turbid by the production of the carbonates.

Carbonic acid is decomposed into carbonic oxide and oxygen by the continued action of the electric spark; the products are, however, induced to reunite by the same agent. It is similarly decomposed, the oxygen becoming fixed or combined, when subjected to a high temperature in contact with carbon, hydrogen, iron, or zinc, or to the electric spark in contact with hydrogen or with some metals. When potassium is heated in an atmosphere of carbonic acid, it becomes incandescent, and abstracts the whole of the oxygen from the gas, the result being potassa and a deposition of carbon. Sodium acts in a similar manner, though less violently. Phosphorus, sulphur, and similar inflammable substances, do not possess this property, and are extinguished if immersed, while burning, in the gas.

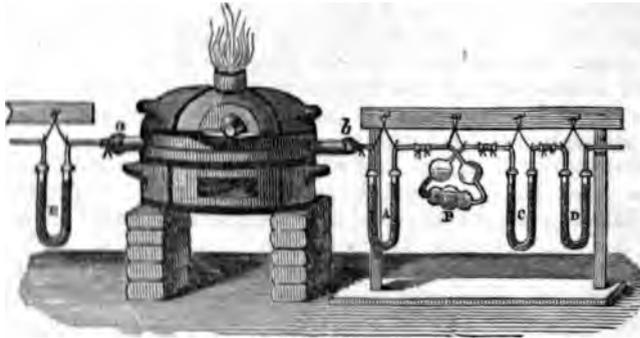
A few words may be said respecting the method employed for determining the composition of carbonic acid, since it may be effected with ease and exactness, and is, both chemically and generally, as important as the determination of the composition of water. A small portion of carbon, as pure and dry as possible,² contained in a little boat or cradle of platinum, is accurately weighed, and introduced into a porcelain tube, *a, b* (Fig. 67), which is heated to redness in a furnace, and contains in *b*, the portion opposite to that in which the carbon is introduced, some porous oxide of copper (retained within a certain distance from the opening of the tube by a plug of asbestos). The extremity, *a* of the tube at which the carbon was introduced, is connected with a gas-holder, from which a

¹ Animals or persons rendered insensible or thrown into convulsions by inhaling this gas, may frequently be restored by sudden immersion in cold water.

² Diamond has been used in the most accurate determinations of this question.

stream of pure oxygen may be supplied, which is dried previously to its entrance into the tube by passing through an U-tube, E, containing fragments of pumice moistened with oil of vitriol. The other extremity of the porcelain tube at which the oxide of copper is situated is connected with a similar U-tube, A, to the other end of which is attached a bulb absorption-apparatus, P, containing solution of

Fig. 67.



potassa; this is again connected with an U-tube, C, containing pumice moistened with strong solution of potassa, and likewise attached to a third tube, D, similar to the first. The bulbs and these two tubes are accurately weighed together before they are attached to the apparatus. The tubes being all securely connected in the usual manner, the oxygen is allowed to enter the apparatus and expel the air slowly. The porcelain tube is then heated to redness, when the carbon soon ignites, and is converted into carbonic acid, which is absorbed by the caustic potassa in the bulb and U-tube, as it is carried into them by the continuous current of oxygen.

A small amount of moisture may be carried off mechanically by the latter in its passage through these tubes; this is retained by the sulphuric acid in the last weighed U-tube as the gas passes off through it into the atmosphere. Should any carbonic oxide be produced in the combustion of the carbon, which is sometimes the case, it is immediately converted into carbonic acid as it comes in contact with the red-hot oxide of copper contained in the end of the tube. The current of oxygen through the apparatus is allowed to continue for some little time after the combustion of the carbon, to insure the perfect collection of the resulting carbonic acid. When the operation is completed, the three tubes are once more weighed together, the amount of carbonic acid produced being indicated by their increase of weight. The small boat is then carefully removed from the tube and reweighed together with any small amount of residue or ash, resulting from the combustion of the carbon, and consisting of the earthy impurities which it may have contained. This weight, deducted from the original weight of the boat and contents, will furnish the amount of pure carbon employed in the experiment.

The weight of the carbonic acid, inferred from the increase in the weight of the absorption apparatus, and divided by the carbon employed in the experiment, gives the quantity of oxygen contained in the gas.

Carbonic acid is a colorless gas. This acid unites with metallic oxides, producing salts which are termed carbonates. It is, however, a very feeble acid, being easily displaced by a great number of other organic acids. The carbonates of calcium have it accompanied by a strong alkaline reaction. The hydrate of carbonic acid does not appear to exist in the free state; it is, however, contained

in the bicarbonates of the alkalis, the general formula for which is MO.CO_2 , HO.CO_2 . Carbonic acid escapes from all its salts, with the exception of those of the neutral carbonates of the alkalis, when they are exposed to the action of heat. When replaced in its combinations by other acids, it escapes with effervescence.

Uses of Carbonic Acid.—Liquid carbonic acid is employed for the production of the solid acid, which, when mixed with ether, or bisulphide of carbon, is a powerful refrigerator, exceedingly important in all experiments on condensation of gases, and without which many of the most interesting results obtained in this direction by Faraday and others, would probably not have been arrived at. Carbonic acid gas is most extensively employed in the preparation of aerated waters. The liquid to be charged with gas is contained in very strong vessels, made of copper, well-tinned, into which the gas is forced with considerable pressure.

Iron must not be employed in the construction of these vessels, since a solution of carbonic acid has considerable action on that metal. The carbonic acid evolved by fermentation, is often employed on a large scale for the preparation of certain carbonates, such as carbonate of lead, bicarbonate of soda, &c.

Carbonic acid is frequently employed by the chemist for replacing the air in vessels or apparatus in which the absence of free oxygen is absolutely necessary (e. g. in the conversion of phosphorus into the allotropic modification). A mixture of carbonic acid with aqueous vapor and nitrogen, disengaged under considerable pressure, has also been employed for extinguishing fires; the disengaging apparatus (the *fire-annihilator*) being furnished with a hose whereby the gaseous mixture may be directed to any particular point.

In medicine, carbonic acid is administered in the form of aerated saline drinks. Alkaline carbonates are also frequently administered.

CARBON AND HYDROGEN.

Light carburetted hydrogen	C_2H_4
Olefiant gas	C_4H_6

All other compounds of carbon and hydrogen, of which there are a great number, fall strictly within the province of organic chemistry.

LIGHT CARBURETTED HYDROGEN, *Marsh gas or Fire-damp.*

C_2H_4 . *Sp. Gr.* 0.556. *Eq.* 16.

§ 125. *Composition by Volume.*—4 volumes of carbon-vapor and 8 volumes of hydrogen condensed to 4 volumes.

This gas, being a product of the decomposition or putrefaction of vegetable matter (wood, &c.) under water, frequently escapes in considerable quantities from the bottom of stagnant pools, or may be made to rise to the surface by stirring the mud about. Hence its name of *marsh-gas*. It may be easily collected in such localities by inverting, over the water where it escapes, a bottle filled with water, in the neck of which is fixed a funnel.

The gas thus obtained contains a considerable amount of carbonic acid and a little nitrogen. It may be purified from the former by agitation with lime-water.

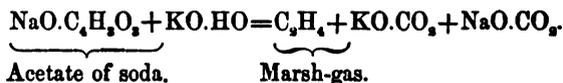
Considerable quantities of the same gas are also found to issue from the earth in some localities, emanating from coal deposits; in working coal-mines it is also frequently met with, inclosed in cavities, rendering the atmosphere inflammable by its admixture, and being hence frequently the cause of dangerous explosions, in consequence of which the name of *fire-damp* was given to it. Serious acci-

dents also happen occasionally, in consequence of the evolution of fire-damp from the cavities existing in coal stored on board ship.

It is also the product of the destructive distillation of coal, and of the action of a high temperature on the vapor of alcohol.

Preparation.—The best method of obtaining this gas is to heat in a copper or coated glass retort, an intimate mixture of 4 parts of dried acetate of soda, 4 parts of fused potassa, and 6 parts of quicklime.

It may be collected over water.



Properties.—Light carburetted hydrogen is a colorless and inodorous gas, burning with a pale blue and white flame; the results of the combustion are carbonic acid and water.¹ It is but very slightly soluble in water. Chlorine has no action upon it in the dark, but when a mixture of the gases is exposed to diffused daylight in the presence of moisture, hydrochloric and carbonic acids are produced:—



When mixed with a small quantity of air, light carburetted hydrogen explodes but feebly or not at all; but if the proportion of air be about the quantity necessary for its complete combustion (about 10 volumes to 1 of the gas), the mixture explodes very violently. As the quantity of air increases beyond that proportion, the explosive power diminishes, until at last the gaseous mixture merely burns round the flame of a candle or lamp.² The frequent and lamentable accidents occurring in coal mines in consequence of the formation of fire-damp, or explosive mixture of air and light carburetted hydrogen, led Sir H. Davy to make a close examination of this gas, with reference to its combustible properties, in connection with some beautiful researches of his on the power possessed by the metals, in consequence of their conducting properties, of cooling down gases in a state of combustion to such an extent as to extinguish flame.

Davy found that flame could not be communicated through a narrow glass tube to an explosive mixture of marsh-gas and air, the cooling power of the sides of the tube preventing the gas from attaining a sufficiently high temperature. Metallic tubes naturally possessed this power to a higher degree, in consequence of their good conducting properties, and it was found that even metallic wires, held within a certain distance of each other, or, more conveniently, wire gauze of a certain fineness, possessed the power of obstructing the passage of flame, or of protecting an explosive mixture from ignition by flame. Thus, by allowing a stream of coal-gas to pass through a piece of moderately fine wire gauze (containing not less than 400 meshes to the square inch), it may be kindled on the upper side without the flame being thereby communicated to it below the gauze. The development of these principles led Davy to the construction of the *safety-lamp*, by the use of which the miner is protected from danger, and at the same time warned of the existence of a pernicious atmosphere. It consists merely of an oil lamp, the wick of which is inclosed in an iron wire gauze cage, of which the upper part is double; a wire, bent into a hook at the upper extremity, passes upwards through the lamp, by which it may be trimmed to some extent without removing the gauze cage.

When this lamp is introduced, while burning, into an inflammable atmosphere, the flame of the lamp will be extinguished, while a bluish flame will be seen

¹ The carbonic acid formed by the explosion of fire-damp in coal mines is technically called "after-damp," and is more fatal to the miners than even the explosion itself.

² No explosion takes place if the volume of air be less than 6 or more than 14 times the volume of the gas.

within the gauze cage, arising from the combustion of the gas as it penetrates; by this, therefore, the miner is immediately made aware of the presence of fire-damp. The lamp may even be allowed to remain in this state in an atmosphere of light carburetted hydrogen until the wire gauze is heated to dull redness by the heat of the burning gases inside; for, although kindled immediately by flame, this gas requires a higher temperature for its ignition than most other inflammable gases. An iron rod heated to dull redness will set fire to olefiant gas, hydrogen, carbonic oxide, &c., while the temperature of iron must be almost a white heat before it will inflame light carburetted hydrogen.

COAL-GAS.

§ 126. The gaseous product of the distillation of coal contains light carburetted hydrogen in much larger proportion than any other gas; it will, therefore, not be out of place to enter here into a brief account of the preparation and nature of coal-gas.

By submitting coal to distillation in closed iron retorts, three principal products are obtained: a dark, oily, viscid fluid, known as coal-tar, containing a variety of substances; an aqueous liquid, containing ammonia and its salts; and a gaseous mixture, the principal constituent of which is light carburetted hydrogen, but which contains besides, variable quantities of olefiant gas, carbonic oxide, hydrogen, carbonic acid, and nitrogen, and smaller quantities of sulphuretted hydrogen, bisulphide of carbon, vapor of volatile liquid hydrocarbons, ammonia, cyanogen, hydrochloric acid, and aqueous vapor. The four first-named products form the main bulk of the gas, together with the vapors of the volatile liquids; the hydrogen and carbonic oxide are evidently produced by the decomposition of moisture in the coal, or of water produced in the distillation, the vapor of which, passing over the red-hot coal, yields these two gases. All coal contains more or less sulphur (generally existing as iron-pyrites), which is converted during the distillation into hydrosulphuric acid, and vapor of bisulphide of carbon.

The nitrogen existing in coal is expelled as ammonia, cyanogen (C_2N), and a combination of the latter substance with sulphur, sulphocyanogen (C_2NS_2); any free nitrogen is due to the atmospheric air contained in the retorts at the commencement of the operation. The only absolutely essential constituents of coal-gas, obtained in the ordinary process of manufacture, are light carburetted hydrogen and olefiant gas. Its illuminating power is mainly owing to the latter, and to the vapors of liquid hydrocarbons which the gas contains, while the light carburetted hydrogen, though burning with but a pale flame, evolves much more heat by its combustion than the olefiant gas, and thus, by imparting a very high temperature to the small particles of carbon separated during the combustion of the illuminating constituents (§ 65), contributes considerably, though indirectly, to the luminosity of the gas-flame.

There are, however, considerable objections to the presence of large quantities of both light carburetted hydrogen and carbonic oxide, as diluents in coal-gas, in consequence of the large amount of carbonic acid generated by their combustion; the excessive amount of heat evolved during the combustion of light carburetted hydrogen is also a great drawback to the use of such gas, containing a large quantity of this constituent, for the illumination of apartments; though, on the other hand, when the gas is employed solely as a source of heat, its value is much increased from the same cause. It would, however, greatly add to the general utility of gas, if the light carburetted hydrogen could be entirely, or in part, replaced by hydrogen, since this gas evolves much less heat in proportion to its volume, and its product of combustion is perfectly innocuous. This object appears to be to a great extent attained, by the application of a new process for the manufacture of gas, which we shall presently notice.

The peculiar property which chlorine possesses, of forming, when mixed with coal-gas, oily substances with those of its compounds to which it owes its illuminating properties, namely, olefiant gas, and the vapors of hydrocarbons, affords a ready means of testing its illuminating power, which is, of course, in direct proportion to the decrease in volume of the gas when mixed with chlorine. From experiments made by Henry, it has been proved that the gaseous products of the distillation of coal differ very considerably at the various periods of the operation. Before the coal arrives at a cherry-red heat, the products consist almost entirely of hydrogen and tar, together with the atmospheric air from the retort. When the retort has attained the stated temperature, illuminating gas passes over, the value of which decreases in proportion to the length of time for which the coal has been heated.

Time of collection.	Spec. grav.	Absorbed by chlorine.	Light carburetted hydrogen.	Carbonic oxide.	Hydrogen.	Nitrogen.
In 100 parts of gas from Wigan cannel coal.						
In 1st hour	0.650	13	82.5	3.2	0	1.3
	0.620	12	72	1.9	8.8	5.3
	0.630	12	58	12.3	16	1.7
3 hours after commencement . . .	0.500	7	56	11	21.3	4.7
10 hours ditto	0.345	0	20	10	60	10

We see from the above that the gas evolved towards the termination of the process, only serves to increase the total volume obtained from the coal, and to deteriorate by dilution the illuminating power of the gas, since that obtained at the expiration of the tenth hour burns with merely a pale blue flame. The large amount of hydrogen found in the last stage of the operation can evidently no longer be produced by the decomposition of water, but must be due to the action of the high temperature upon the compounds of carbon and hydrogen which have been proved to be resolved into their elements at a high red heat (p. 139). The carbon thus liberated is found deposited on the sides of the retort as an exceedingly hard and dense crust, known by the name of gas-carbon (p. 141). This kind of decomposition cannot, under any circumstances, be carried on, save the gas as it is evolved from coal, in large retorts, must always possess a red-hot surface, it may, however, be much diminished by a careful regulation of the temperature.

The retort used should be the best for the manufacture, and the Scotch or iron retort. The coal should be as dry as possible, and when subjected to heat should be raised as rapidly as possible to a cherry-red heat, at which temperature it should be uniformly maintained throughout the distillation. The retort should be covered when experiments have shown that the illuminating power is at its greatest amount.

The retort may be a cylinder, or four times spherical, cylindrical, or slight conical shape, and be connected with necks, tubes which conducting pipes may be attached to, and extend to the outside, where a large

The retort should be covered when experiments have shown that the illuminating power is at its greatest amount.

The retort should be covered when experiments have shown that the illuminating power is at its greatest amount.

quantity of tar and ammoniacal liquor is deposited from the gas as it passes from the retorts. From the hydraulic main the gas is conducted into a series of iron tubes, which are kept cool by water, and in which the chief part of the easily-condensable impurities is separated from the gas.

In some of the large works the gas is allowed to pass from the condenser into a washing-apparatus, consisting of a very long iron case furnished with three or four shelves, placed at intervals of about one foot, and attached alternately to either side of the case; water is allowed to trickle over these shelves, and a large surface being thus exposed to the action of the gas flowing in an opposite direction, a large quantity of the gaseous impurities is absorbed by it.

In another ingenious arrangement, termed the *scrubber*, the gas is allowed to enter at the bottom of a tall cylindrical case, containing perforated shelves charged with fragments of coke, over which water is allowed to trickle; in this way a still further purification of the gas may be effected.

When the gas leaves the washing-apparatus, it has still to be purified from the remainder of the incondensable constituents, which are highly detrimental to its quality, such as ammonia, sulphuretted hydrogen, &c. The method exclusively employed, till very recently, for the removal of these obnoxious impurities, was that of bringing the gas into contact with slaked lime, or milk of lime. When milk of lime is used, the gas is allowed to pass through a considerable bulk in very small bubbles, the liquid being, at the same time, continually agitated with a rouser or stirrer. The chemical action of this substance is, however, insufficient to effect perfect purification of the gas; the most effectual means of retaining not only the sulphur compounds, but the ammoniacal salts, is evidently the use, as purifiers, of salts of earths, or other metallic oxides, which will effect double decomposition, and produce non-volatile compounds. Sulphate of lead has been employed as a purifier, sulphate of ammonia and sulphide of lead being the chief results of its action on the gas; it is, however, necessary to use lime together with this salt, in order to remove the carbonic acid.

The sulphates of manganese and iron are more efficacious, but the best purifying medium known at present appears to be that which is now introduced into several large metropolitan gas-works, namely, sawdust, saturated with chloride of calcium. The purifying material may, after it has been employed, be worked with advantage for several important commercial chemicals, such as sulphate and muriate of ammonia, and Prussian blue, &c.

After this purification, the gas passes directly into the gasometers, whence it is distributed to the various mains.

The secondary products in the manufacture of gas are of considerable commercial importance. The tar, by distillation, furnishes a liquid known as *coal-tar-naphtha*, which is a mixture of various acid, basic, and neutral hydrocarbons, the description of which falls within the province of organic chemistry. The most important of these substances is a volatile liquid known as *benzol* ($C_{12}H_6$), which has lately been employed as an illuminating material, and for several other purposes. The residue after the distillation of tar is termed *pitch*.

The ammoniacal liquor, which is very rich in carbonate of ammonia, is employed for the preparation of sulphate of ammonia, and chloride of ammonium. Other chemical products (*e.g.* Prussian blue) are also obtained from this liquor.

When lime is used as a purifying agent, it is withdrawn from the purifiers after a certain time, and is used as a manure under the name of *gas-lime*.

§ 127. ANALYSIS OF COAL-GAS.—The rigorous analysis of gases requires so much accuracy of manipulation, and involves so many operations peculiar to itself, that it almost deserves to be considered a separate branch of practical chemistry. Sufficient has been said in the article on the measurement and absorption of gases (§ 86), to give a general idea as to the manner in which analyses of gas are con-

ducted. We shall therefore confine ourselves in this place to an outline of the method usually pursued in the examination of coal-gas.

The following are the substances usually determined:—

Olefiant gas	} <i>Illuminating constituents.</i>
Vapors of hydrocarbons	
Light carburetted hydrogen.	
Hydrogen.	
Carbonic acid.	
Carbonic oxide.	
Nitrogen.	

A measured volume of the gas standing over mercury, is agitated with solution of potassa, allowed to stand for some time, and again measured.

The difference of volume indicates the amount of carbonic acid.

The residual gas is transferred, in the pneumatic (water-) trough to a graduated tube, carefully measured, mixed with half its volume of pure chlorine, and allowed to stand for twenty-four hours in a dark place. The tube is then placed in a jar containing solution of potassa, and agitated for some time to remove the excess of chlorine. The residue is then measured.

The difference between this volume and the preceding, indicates the volume of olefiant gas and vapors of hydrocarbons (and hence is a measure of the illuminating value of the gas).

Another method consists in passing up a pellet of coke, moistened with fuming sulphuric acid (in the manner described, § 36), into a known volume of the dry gas over mercury, and afterwards removing any acid vapor by a similar pellet of fused potassa.

The remaining gas, or a measured portion of it, is introduced into a small tube, the closed end of which is bent downwards, standing over mercury. (All moisture must be removed from the mercury with blotting-paper, and from the gas by prolonged contact with pellets of fused hydrate of potassa.) A small pellet of potassium is introduced into the closed extremity of the tube, and gently heated, so that it may absorb the carbonic oxide.

The gas is then again transferred to a graduated tube, over water, and measured. The difference in volume shows the amount of carbonic oxide.

The remaining gas, after the removal of the carbonic oxide, is introduced into an eudiometer (§ 32), mixed with a measured quantity (about twice the volume of the gas) of oxygen, and exploded by the electric spark, over mercury.

The volume of the residual gas (oxygen, nitrogen, carbonic acid) is carefully noted, and agitated with solution of potassa, which absorbs the carbonic acid, the volume of which is equal to that of the light carburetted hydrogen.

The remainder is exposed to the action of phosphorus, over water, for 24 hours; the amount of oxygen absorbed is then deducted from the total quantity employed, in order to ascertain the amount consumed in the combustion. By deducting from this quantity twice the volume of the light carburetted hydrogen, we obtain the measure of oxygen consumed by the free hydrogen, the volume of which is of course double that of the oxygen.

Finally, the residual consists of nitrogen.

In the above sketch, we have, for the sake of simplicity, omitted to mention the corrections for temperature, barometric pressure, and aqueous vapor, so necessary in all analyses of gaseous mixtures. For the methods of effecting these corrections we refer to § 5.

§ 125. *Coal gas*—Recent gas, coal oil, and impure oils of various kinds, which are not adapted for burning are sometimes used for the production of gas. Experiments made by Henry, have shown that the gas obtained by distilling bituminous coal at a comparatively low temperature (a dull red heat) possesses illu-

minating powers far superior to coal-gas, the amount of gaseous matter absorbed by chlorine being considerably greater; a portion of this consists of a peculiar gas discovered by Faraday, to be presently described (§ 129). The gas is prepared from oil by allowing the latter to flow into a retort (similar to a coal-gas retort) filled with bricks or lumps of coke, heated to dull redness. Gas is also obtained for illuminating purposes from resin, which is first fused, and then, like the oil, allowed to fall upon heated lumps of coke or brick.¹ Even the gases obtained by the distillation of animal matters, flesh, bones, soap-waste, and in the manufacture of bone-black, are here and there used for illuminating purposes.

WATER-GAS.—Among various more recent methods of preparing illuminating gas, we may mention that which consists in passing steam over heated charcoal or coke, and conducting the resulting gases, consisting of hydrogen, carbonic oxide, and carbonic acid, together with a considerable quantity of aqueous vapor, into a second retort, in which illuminating gas is being generated, either from coal or resin. The great advantages of this process appear to be the following: 1. That the olefiant gas and vapor of hydrocarbons are rapidly removed from the retort by the current of water-gas, and are therefore not exposed to a temperature sufficiently high to decompose them, as is generally the case; 2. That the aqueous vapor appears to be decomposed in coming in contact, at an elevated temperature, with the tarry hydrocarbons, in such a manner as to convert their carbon into carbonic oxide, and to liberate the hydrogen, which advantageously replaces, as above noticed, a part of the light carburetted hydrogen in ordinary gas; 3. That the carbonic acid produced in the first retort is reduced in the second to carbonic oxide, by contact with the carbonaceous matter at a high temperature; 4. That certain coals which generally yield a gas burning with a smoky flame, from a superabundance of carbon, may be made to furnish a gas sufficiently diluted for illuminating purposes.

It is at once apparent that the quantity of gas obtained by this process from a given amount of coal is considerably increased, as is also the *total* illuminating power; although the amount of light obtained by the combustion of a given volume of this gas must obviously be less than that yielded by an equal volume of coal-gas.

OLEFIANT GAS, BICARBURETTED HYDROGEN.

C_4H_4 . Eq. 28. Sp. Gr. 0.985.

Composition by Volume.—2 volumes of carbon-vapor and 2 volumes of hydrogen condensed to 1 volume.

§ 129. This carburetted hydrogen is produced in variable quantities, as already stated, by the distillation of coal, the luminosity of coal-gas being mainly dependent upon its presence.

Preparation.—It may be obtained by heating together, in a capacious retort, a mixture of 1 measure of alcohol and 3 measures of concentrated sulphuric acid. The mixture soon blackens, and effervescence ensues, when the temperature must be moderated, or the action becomes very intense. The gas may be obtained in larger quantity and of greater purity, according to the directions of Graham, by mixing, in a capacious flask, 28 ounces of water with twice their volume of oil of vitriol, and adding to the diluted acid, while hot, 24 measures of alcohol. The mixture is allowed to stand for some hours, and then maintained in a state of gentle ebullition.

¹ The furnaces are so arranged that the resin is melted in a reservoir, placed above the retort, and exposed to the waste heat of the fire. A pipe, provided with a plug or stopcock, connects the cistern with the retort; the melted resin is supplied to the latter through this pipe.

The principal result of the action of sulphuric acid upon alcohol in this instance is the conversion of the latter into olefiant gas and water:—



There are, however, several secondary reactions, resulting in the decomposition of the sulphuric into sulphurous acid, the formation of carbonic acid, and of a considerable quantity of ether.¹ It is therefore necessary to submit the gas obtained to purification, which is effected by passing it first through water, to retain the principal quantity of ether and the alcohol which distils over unchanged,² and afterwards through a solution of potassa, to retain the sulphurous and carbonic acids, and finally through oil of vitriol to remove water. The gas may be collected over water, which absorbs about one-eighth of its volume.

Properties.—Olefiant gas is colorless, and has a peculiar alliaceous odor. It burns with a brilliant white flame, requiring three times its volume of oxygen for complete combustion.

It may be converted by cold and pressure into a colorless liquid, which cannot be solidified at the lowest attainable temperature. Fuming sulphuric acid and pentachloride of antimony have the power of absorbing considerable quantities of this gas, producing peculiar compounds.

It is generally found that these liquids leave certain impurities in olefiant gas uncondensed, which consist principally of light carburetted hydrogen gas.

Olefiant gas burns in an atmosphere of chlorine, yielding hydrochloric acid and carbon. When mixed with an equal volume of that gas in a moist state, it combines with it to produce an oily liquid of the formula $\text{C}_2\text{H}_4\text{Cl}_2$ (see Chloride of Carbon, § 131), to which the name *Dutch liquid* has been given, in consequence of its having been discovered by the associated Dutch chemists, who gave the name of olefiant gas to bicarburetted hydrogen, on account of this property.³

When olefiant gas is passed through a porcelain tube, heated nearly to whiteness, it is decomposed into carbon and hydrogen; if a lower temperature be employed, only a part of the carbon is separated, light carburetted hydrogen being formed.

BICARBURETTED HYDROGEN OF FARADAY, or Gas of Oil.



This gas has already been referred to as one of the products of the destructive distillation of fatty oils. It may be liquefied at a temperature of 0°F. (-18°C.), or by subjecting oil-gas to considerable pressure. Its specific gravity is double that of olefiant gas. It is only slightly soluble in water, but more so in alcohol and fatty oils; fuming sulphuric acid absorbs as much as 100 times its volume. It has already been stated that chlorine unites with all the compounds of carbon and hydrogen that possess the same percentage composition as olefiant gas.

This gas produces a compound with chlorine somewhat similar to Dutch liquid. When inflated, it burns with a brilliant light; it requires for its combustion 6 volumes of oxygen.

¹ At times also the olefiant gas is contaminated by light carburetted hydrogen, and also by higher compounds of carbon and hydrogen.

² A specimen of "etherical" gas, formed in the same way, condenses in the first wash-bottle.

³ Berzelius has also given the name *Dutch* to this gas, from *Daan*, the source of an oil.

⁴ The name *gas of oil* has also been given to this gas, from *Daan*, the source of an oil; and it is also called *gas of oil*, because 4 volumes of carbon-vapour and 4 volumes of hydrogen condensed to 1 volume.

CARBON AND NITROGEN.

BICARBIDE OF NITROGEN, CYANOGEN.

C₂N or Cy. Eq. 26. Sp. Gr. 1.806.

Composition by Volume.—1 volume of cyanogen contains 2 volumes of carbon-vapor and 1 volume of nitrogen.

§ 130. This substance is of considerable importance, inasmuch as it is the type of those bodies known as compound salt-radicals (§ 12), and was the first of these discovered, in 1814, by Gay-Lussac.

Cyanogen is always produced, in combination with an alkali-metal, when nitrogenized organic matter is heated with an alkaline carbonate.

Cyanide of potassium is formed when nitrogenized organic bodies are heated with potassium, or when nitrogen (or atmospheric air) is passed over charcoal, in presence of potassa, at a high temperature. It is probably by the latter method that cyanide of potassium is formed in the blast-furnaces in which iron is reduced from its ores.

When ammoniacal gas is passed over charcoal at a high temperature, cyanide of ammonium is formed.

Preparation.—Cyanogen is prepared by heating pure dry cyanide of mercury in a retort or tube of hard glass; the gas may be collected over mercury, or, with some loss, by downward displacement.

The cyanide of mercury is not entirely volatilized in this experiment, a small quantity of a brown substance is left, which has the same percentage composition as cyanogen, and is termed *paracyanogen*.

The cyanide of mercury must not contain any oxycyanide, or the cyanogen will be contaminated with carbonic acid and nitrogen.

If any moisture be present in the cyanide, carbonate of ammonia and cyanide of ammonium will be formed.

Properties.—Cyanogen is a colorless gas, having a peculiar and characteristic pungent odor. It condenses to a colorless liquid at the ordinary temperature, under a pressure of 4 atmospheres. Liquid cyanogen may be obtained by heating cyanide of mercury in one limb of a closed bent tube, the other limb of which is surrounded with a mixture of ice and salt. The specific gravity of liquid cyanogen is 0.9. It may be solidified by the aid of a mixture of solid carbonic acid and ether.

Cyanogen is combustible; it burns with a remarkable peach-colored flame, yielding carbonic acid and nitrogen. A mixture of cyanogen and oxygen is exploded by contact of flame, or of the electric spark.

Water dissolves about 4 times its volume of cyanogen, but it is much more soluble in alcohol, which is capable of absorbing about 25 volumes. The gas may be easily expelled from these solutions by heat.

An aqueous solution of cyanogen may be kept unchanged for a long time in the dark, but, if exposed to light, it deposits a brown matter, containing the elements of cyanogen and water, while the solution contains carbonate of ammonia (NH₄O.CO₂), cyanide of ammonium (NH₄C₂N), oxalate of ammonia (NH₄O.C₂O₂), formiate of ammonia (NH₄O.C₂HO₂), and urea (C₂H₄N₂O₂). It will be seen that these various compounds contain only the elements which exist in cyanogen and water; the explanation of this most interesting decomposition belongs strictly to organic chemistry.

Cyanogen is absorbed by solutions of the alkalis, which it decomposes in the same manner as chlorine, giving rise to cyanides of the metals, and cyanates of the alkalis.



Cyanogen combines directly with potassium and sodium at a slightly elevated temperature.

Combinations of cyanogen are known, with oxygen, hydrogen, chlorine, bromine, iodine, sulphur, and most metals. The history of these compounds is, however, so interwoven with that of many others belonging to the department of organic chemistry, that its consideration belongs more appropriately to that branch of the science.

We subjoin a list of some of the principal compounds of cyanogen.

Cyanic acid	CyO
Fulminic acid	Cy ₂ O ₂
Cyanuric acid	Cy ₃ O ₃
Hydrocyanic, or prussic acid	HCy
Gaseous chloride of cyanogen	CyCl
Liquid "	"	Cy ₂ Cl ₂
Solid "	"	Cy ₂ Cl ₂
Bromide	"	CyBr
Iodide	"	CyI
Bisulphide	" (sulphocyanogen)	CyS ₂
Ferrocyanogen	Cy ₆ Fe
Ferricyanogen	Cy ₆ Fe ₃
Cobalticyanogen	Cy ₆ Co ₃
Manganicyanogen	Cy ₆ Mn ₃
Chromicyanogen	Cy ₆ Cr ₃
Platinocyanogen	Cy ₆ Pt
Palladiocyanogen	Cy ₆ Pd
Iridiocyanogen	Cy ₆ Ir

The last nine compounds are themselves quasi-elements, or compound salt-radicals, which have not been isolated, but are known to exist in a well-defined series of compounds.

Mellon, C₆N₆, is another salt-radical, the description of which must be reserved for organic chemistry.

CARBON AND CHLORINE.

Protochloride of carbon	C ₂ Cl ₄ (4CCl)
Sesquichloride of carbon	C ₂ Cl ₆ (2C ₂ Cl ₃)
Bichloride of carbon	C ₂ Cl ₄ (2CCl ₂)

§ 131. These elements do not unite directly, but their compounds are produced by the action of chlorine on combinations of carbon with other non-metallic substances. The description of their formation, though more frequently included in organic chemistry, may be briefly entered into here, since it is in close connection with the subject of carbohydrogens, of which we have just been treating.

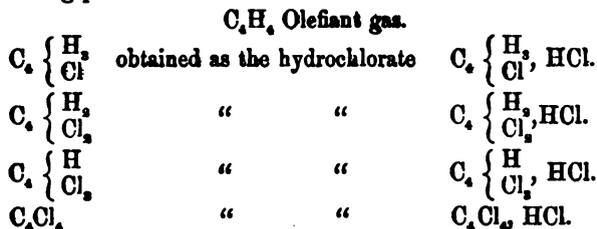
It has already been mentioned, that when olefiant gas is mixed with an equal volume of chlorine, an oily substance, known as *Dutch liquid*, is obtained. It is a colorless liquid, possessing a peculiar, sweet, agreeable odor; its specific gravity is 1.24; it boils at 67°.6 F. (84°.5 C.), yielding a vapor of specific gravity 3.448. The empirical formula is C₂H₂Cl₂; but a closer study shows that it must be represented by the formula C₂H₂Cl.HCl, being, in fact, a compound of what is called the *chloride of acetylene* (or dichloroacetylene), C₂H₂Cl, with hydrochloric acid; and, indeed, if Dutch liquid is subjected to the action of an alcoholic solution of potassa, chloride of potassium is produced by the decomposition of the hydrochloric acid, and the body C₂H₂Cl obtained, as a very volatile, limpid liquid.

If Dutch liquid be submitted to the action of a current of dry chlorine, it absorbs a considerable quantity; a second equivalent of hydrogen, existing originally in the olefiant gas, is converted into hydrochloric acid, and replaced by an equivalent of chlorine, the substance $C_2H_2Cl_2.HCl$ being produced, from which an alcoholic solution of potassa separates the body $C_2H_2Cl_2$.

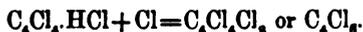
The hydrochlorate of this second substance is again acted upon in a similar manner by chlorine gas, a third equivalent of hydrogen is abstracted and replaced by chlorine; the resulting compound is the hydrochlorate of a third substance in this series, containing now only one equivalent of hydrogen, its formula being $C_2HCl_3.HCl$. (This compound may likewise be decomposed by potassa in a similar manner to the others.) This substance, once more acted upon by chlorine, yields a compound of the formula C_2HCl_4 , or $C_2Cl_4.HCl$, which is therefore the hydrochlorate of the quadrichloride, or what was originally called the protochloride of carbon, C_2Cl_4 . By the action of alcoholic potassa, this chloride may be separated from the hydrochloric acid; we shall proceed to its description immediately.

When, finally, this last hydrochlorate (C_2HCl_4) is submitted to the action of excess of chlorine under the influence of the sun's rays, the last equivalent of hydrogen which it contains is replaced by chlorine, and the sesquichloride of carbon $C_2Cl_6=2(C_2Cl_3)$ is obtained.

In the above reactions, therefore, the hydrogen in olefiant gas is gradually replaced, equivalent after equivalent, by chlorine, hydrochlorates of the various substances being produced as follows:—



Finally, the hydrochlorate of the last substance yields up its hydrogen for chlorine, thus:—



This view regarding the constitution and formation of the chlorides of carbon has been established by the observation of their vapor-densities.

PROTOCHLORIDE OR QUADRICHLORIDE OF CARBON.

C_2Cl_4 . *Sp. Gr.* 1.5.

§ 182. This compound is obtained by passing the vapor of sesquichloride of carbon through a redhot glass tube, filled with fragments of glass. Chlorine is liberated in this reaction, and a colorless liquid is obtained, which, when purified, boils at 240° F. (120° C.), and has a composition corresponding to equal equivalents of chlorine and of carbon, whence its name, protochloride; its true formula is, however, proved to be C_2Cl_4 , by an examination of its vapor-density, which was found to be 5.820 by direct experiment:—

8 volumes carbon-vapor . . .	3.371
8 “ chlorine . . .	19.523
	22.894
Density	$\frac{22.894}{4} = 5.724.$

This, therefore, establishes its character as a derivative of olefiant gas, C_2H_4 .

SESQUICHLORIDE OF CARBON, C_3Cl_4 . *Sp. Gr.* 2.

This substance is obtained by acting upon Dutch liquid with chlorine, under the influence of solar radiation, as long as any more of the gas is absorbed. It is a white crystalline solid, of a peculiar aromatic odor, somewhat resembling camphor. It may easily be purified by crystallization from boiling alcohol. It is volatile, fusing at 320° F. (160° C.), and boiling at 365° F. (185° C.) The density of its vapor is 8.157.

PERCHLORIDE OF CARBON, C_2Cl_4 . *Sp. Gr.* 1.6.

Regnault obtained this substance by the action of excess of chlorine upon chloroform (C_2HCl_3), and regards it as the final product of the substitution of chlorine for hydrogen in light carburetted hydrogen, C_2H_4 , analogous to the product C_2Cl_4 from olefiant gas, C_2H_4 ; since, by the action of excess of chlorine, in sunlight, upon light carburetted hydrogen, he obtained, besides chloroform and other compounds of a similar nature, a portion of the compound C_2Cl_4 , or perchloride of carbon.

It is also obtained by passing a mixture of chlorine gas and bisulphide of carbon vapor through a redhot porcelain tube containing fragments of porcelain. Chloride of sulphur is simultaneously produced. The perchloride of carbon is a colorless, limpid liquid, possessing a peculiar alliaceous odor, and boiling at 172° F. (78° C.) Its vapor-density is 5.415.

Regnault obtained another sesquichloride of carbon, the vapor-density of which was only 4.082, by passing the vapor of the above chloride through a tube heated to low redness.

By the action of chlorine upon the crystalline hydrocarbon *naphthaline*, already mentioned, another crystalline chloride of carbon, of the formula $C_{10}Cl_4$ has been obtained.

Carbon with Bromine and Iodine.—No compounds of carbon with bromine and iodine have been obtained. Olefiant gas unites with them to produce compounds analogous to Dutch liquid; the bromine compound may be robbed of one other equivalent of hydrogen, but the action does not proceed further; with iodine, not even the second substance can be obtained.

CARBON AND SULPHUR.

BISULPHIDE OF CARBON, OR SULPHO-CARBONIC ACID.

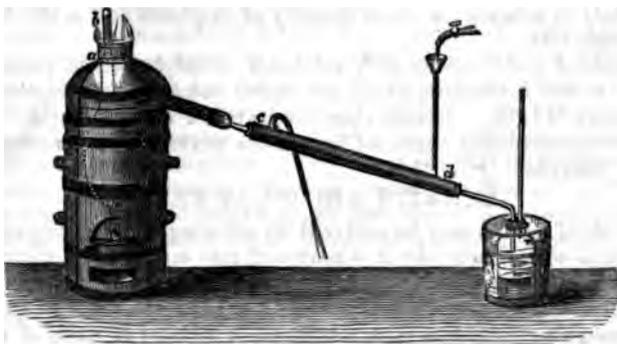
 CS_2 . *Eq.* 38. *Sp. Gr.* 1.263.

§ 133. When a mixture of sulphur and carbon is heated, they do not unite; but if sulphur-vapor be passed over charcoal in a porcelain tube heated to bright redness, they combine, producing a substance analogous in composition to carbonic acid.

Preparation.—The best method of obtaining the bisulphide of carbon is to fill a large earthenware tubulated retort *a* (Fig. 68) with small dry fragments of charcoal; into the tubulure of the retort is fitted with luting a porcelain tube *b*, passing nearly to the bottom of the retort. The latter is heated in a furnace capable of surrounding its body; the neck is connected with a Liebig's condenser *c*, *d*, in which the water is constantly changed; the extremity of its conducting-tube passes down to the lower part of a bottle, which is also surrounded by cold water, and contains itself a little of that liquid. When the retort is raised to the proper temperature, fragments of sulphur are gradually introduced through the tube, the opening of which is immediately closed with a stopper after each introduction. The sulphur being at once converted into vapor, passes over the

redhot charcoal, and is converted into bisulphide of carbon, which condenses in the receiver.

Fig. 68.



The product thus obtained generally contains a little excess of sulphur in solution, besides the water placed in the receiver to retard its evaporation. It may be purified from the former by rectification over a water-bath, when the sulphur remains behind. Digestion over fused chloride of calcium, and subsequent rectification, will free it from water.

This substance may also be prepared by heating, in an earthenware retort, a mixture of charcoal and metallic sulphides (iron or copper pyrites), which part with their sulphur pretty readily.

Properties.—Bisulphide of carbon is a colorless, very volatile liquid, refracting light powerfully. It possesses a fetid odor. It boils at 113° F. (45° C.), and by the rapidity with which it evaporates, especially *in vacuo*, is capable of producing a great degree of cold.¹ The density of its vapor is 2.67. Bisulphide of carbon is but very slightly soluble in water, but dissolves to any extent in alcohol and ether. It is exceedingly inflammable, burning with a pale-blue lambent flame; the products of combustion are carbonic and sulphurous acids. If a few drops of bisulphide of carbon are introduced into a vessel containing oxygen or nitric oxide, its vapor diffuses itself at once through the gases, producing very combustible mixtures, which burn with a brilliant flash of light and explosion, when flame is applied.

Sulphur, phosphorus, and iodine are easily soluble in bisulphide of carbon; the two former substances are frequently crystallized (as specimens) from their solution in this liquid, by very gradual spontaneous evaporation.

If a solution of phosphorus in bisulphide of carbon be poured upon a piece of paper, the film of phosphorus, deposited by the almost instantaneous evaporation of the solvent, will be acted upon with such rapidity by the oxygen of the air, that the heat generated will cause it to burst into flame.

This solution is employed in electrotyping objects, which are coated by its means with a film of phosphorus, and thereby rendered capable of receiving a metallic covering when introduced into a solution of copper.

The vapor of bisulphide of carbon consists of 2 volumes of carbon-vapor and 1 volume of sulphur-vapor, condensed to 2 volumes; being in this respect analogous to carbonic acid.

It has already been stated that when bisulphide of carbon and chlorine are

¹ A mixture of solid carbonic acid and bisulphide of carbon produces the most intense cold.

passed together through a redhot tube, the former is converted into chloride of sulphur and perchloride of carbon.

When kept for a long time under water, in vessels containing air, bisulphide of carbon acquires a yellow color, from partial oxidation and separation of sulphur which is held in solution; a small quantity of sulphuric acid is also formed, besides carbonic acid.

Bisulphide of carbon unites with sulphides or sulphur-bases, producing salts analogous to the carbonates, which are called *sulpho-carbonates*, their general formula being $MS.CS_2$. It may therefore be called a sulphur-acid. Some metallic oxides are gradually converted by it into a mixture of carbonate and sulpho-carbonate, thus:—



Bisulphide of carbon may be analyzed by allowing it to undergo combustion with chromate of lead, whereby it is converted into carbonic and sulphuric acids, the former being determined in the ordinary manner, the sulphur by difference. Or, the latter may be directly determined by passing the vapor of bisulphide of carbon through a combustion-tube, containing a mixture of oxide of copper and carbonate of soda, heated to redness. The carbon escapes as carbonic acid, accompanied by an equal volume of the gas evolved by the action of the sulphuric acid produced, upon the carbonate of soda.

In preparing bisulphide of carbon by passing sulphur-vapor through a redhot tube containing charcoal, the residual portion of the latter is found to contain some sulphur which cannot be expelled by heat.

Berzelius considered that there was a solid compound of sulphur with the carbon, formed in this experiment.

When bisulphide of carbon-vapor is passed over a quantity of redhot iron or copper, insufficient for its perfect decomposition, it is converted into a rose-colored, thin, sharp-tasting liquid, which is said to contain probably *protosulphide of carbon*.

CARBON AND THE METALS.—Carbon, though possessing no active affinity for metals, may be made to unite with several, particularly with iron, producing metallic *carburets* or *carbides*. These compounds are easily decomposed into carbonic acid and the metallic oxides, when heated in contact with air.

BORON.

Sym. B. Eq. 10.9.

§ 134. In 1808, Gay-Lussac and Thénard, and directly afterwards, Davy, decomposed boracic acid (discovered in borax by Homberg, in 1702) into boron and oxygen.

The first-named chemists obtained this element by heating boracic acid and potassium; while Davy procured it by the action of a powerful voltaic battery on boracic acid.

Boron is one of the rarer non-metallic elements; it exists in nature only in the form of boracic acid (in hot springs and lagoons), and in combinations of this acid with metallic oxides, as tincal (crude borax) datolite, boracite, &c.

Preparation.—When vitrified boracic acid is powdered and heated in a tube of glass, iron, or copper, with an equal weight of potassium, cut up into small pieces, the oxygen in the acid is seized by the metal, and a portion of boron thus reduced, while borate of potassa is formed. This may be removed by treatment with hot water, and the boron is obtained in a state of powder.

The best method of obtaining boron is to prepare the double fluoride of boron and potassium ($3KF \cdot 2BF_3$), by saturating hydrofluoric acid with boracic acid, and then gradually adding fluoride of potassium. The difficultly soluble double compound thus produced is collected and dried at a temperature nearly approaching to redness.

This compound is then powdered, and introduced into an iron tube closed at one end, together with an equal weight of potassium, whereupon heat is applied sufficient to melt the latter, and the mixture of the two substances is effected by stirring with an iron wire. Upon the mass being exposed to a red heat, the potassium abstracts the fluorine. The fluoride of potassium may afterwards be removed by heating the mass with a solution of chloride of ammonium, which converts the free potassa into chloride of potassium, and thus prevents the oxidation of the boron, which takes place in the presence of fixed alkali; the chloride of ammonium adhering to the boron may be afterwards removed by treatment with alcohol.

Properties.—Boron is obtained by the above methods as a dark, greenish-brown powder, both tasteless and inodorous, and very similar in external characters to carbon.

Boron is not dissolved by any simple solvent. Oxidizing agents, such as nitric acid, dissolve it in the form of boracic acid; hydrofluoric acid converts it into fluoride of boron, hydrogen being evolved.

It does not fuse when exposed to a red heat in hydrogen, but may be liquefied between the poles of a galvanic battery. Boron, like carbon, has never been converted into vapor. It burns with a bright light and scintillation, if heated in air or oxygen, boracic acid being produced, which is the only oxide of boron known.

When heated with nitrate of potassa, it is rapidly oxidized, being converted into borate of potassa; the action is sometimes accompanied by violent deflagration. Borate of potassa is also formed when boron is heated with carbonate of potassa, carbon being separated.

Boron unites with considerable energy with chlorine and sulphur; its combination with fluorine has already been referred to.

BORACIC ACID, BO_3 . *Eq.* 34.9. *Sp. Gr.* 1.83.

§ 135. This acid occurs, as already stated, in several minerals, particularly as *tincal*, or crude baborate of soda (borax), which is found in the form of incrustations in the beds of small lakes in Thibet, where it is dug up during the hot season.¹

The greatest quantity of this acid is obtained from the volcanic districts of Tuscany, where numerous jets of vapor (*suffioni*) ascend in thick volumes into the air, charged with boracic acid, which the vapor holds in mechanical suspension; the apertures whence the vapor escapes are exposed in some places, and in others are covered by small, muddy lakes (*lagoons*).

It appears that the acid is brought up to the surface by the water in these lakes, which penetrates occasionally into the mouths of the apertures, and dissolves out the acid principally deposited there by the vapor as it makes its escape. Advantage is taken of this fact for obtaining boracic acid from these jets of vapor, in the following manner:—

A series of *artificial lagoons*, in connection with each other, is constructed of rough brickwork lined with clay, over the mouths of one or more fissures. They are generally built one above the other, on the side of a hill, the upper one being supplied with water from neighboring springs, which, when partly saturated

¹ Small quantities of boracic acid have been detected in several mineral waters in France.

there, is allowed to run into the lower lagoon, and subsequently from thence to another, and so on until it has become sufficiently impregnated with acid from the vapors escaping from the earth at the bottom of these reservoirs, to pay the expense of working. When withdrawn from the lowest lagoon, the liquor is allowed to clarify by standing, and is then evaporated in leaden pans, a quantity of sulphate of lime, which is deposited during the evaporation, being removed with rakes. When a liquor of the spec. grav. 1.07 to 1.08 is obtained, it is transferred to round wooden tubs, lined with lead, where the acid is allowed to crystallize out; it is afterwards drained in a basket, and dried in chambers heated by steam.¹

The boracic acid thus obtained is very impure, containing only about 76 or 77 per cent. of the acid: its chief impurities are the sulphates of ammonia, and the metallic oxides. This crude acid is employed for the preparation of borax, the manufacture of which is described § 173.

Pure boracic acid is prepared by dissolving 1 part of pure baborate of soda in 2½ parts of water, and adding hydrochloric acid until the liquid is powerfully acid. As the solution cools, the boracic acid crystallizes out in small plates, while chloride of sodium remains in solution. The crystals are washed with a little cold water, and then recrystallized from boiling water.

Properties.—Boracic acid crystallizes in thin, colorless, lustrous plates, which contain 43.6 per cent. of water of crystallization. When heated, they first part with their water, and then fuse to a colorless liquid, solidifying upon cooling to a very hard, brittle, transparent, colorless glass, which becomes opaque when kept for some time, even in hermetically-sealed tubes, in consequence, apparently, of the arrangement of the atoms in the form of crystallization proper to the ordinary temperature.

Boracic acid volatilizes when exposed to a very high temperature;² it passes off in considerable quantity with the vapor of water, or of alcohol, being deposited again upon a cool surface in small, colorless, micaceous plates. It is not corrosive; its taste is not acid, but somewhat bitter; its action upon litmus is not powerful; like carbonic acid, it imparts to it a wine-red tint; it turns turmeric brown, in a similar manner to the alkalies.

In its affinities, it is slightly more powerful than carbonic acid, which it replaces in its combinations. Crystallized boracic acid contains three equivalents of water, one of which is constitutional; its formula is therefore $\text{HO} \cdot \text{BO}_2 + 2\text{Aq}$. One part of the acid dissolves in 25.66 parts of water at 60° F. (15°.5 C.), and in 2.97 at 212° F. (100° C.) It is soluble in alcohol, its solution burning with a green flame.

Boracic acid has the property of imparting to many substances a high degree of fusibility, uniting with them generally to produce a glass; it is to this property that baborate of soda owes its application as a flux (borax, § 58).

Boracic acid unites with metallic oxides to produce *borates*. Though so feeble an acid that it only replaces carbonic acid at ordinary temperatures, it has the power of expelling all acids volatile at a red heat. Most borates fuse to transparent glasses, which possess the property of dissolving many metallic oxides, yielding with them various colors. With the exception of the alkaline borates, all salts of this acid are soluble with difficulty in water.

¹ Since fuel is very scarce in Tuscany, the liquor is evaporated, and the crystals are dried, by the heat of the vapor from the *suffioni*.

² When the solutions of certain metallic oxides in fused boracic acid are exposed to a very high temperature, the boracic acid is gradually volatilized, and the oxides deposited in a crystalline state. By this method, several crystallized minerals have been artificially produced, which possess all the properties of their natural prototypes. Thus *spinelle* ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) has been obtained by dissolving alumina and magnesia in fused boracic acid.

BORON AND NITROGEN.—A porous white substance may be produced by heating together two parts of chloride of ammonium and one part of dried borax, which appears to be *nitride of boron*, having the formula BN. It is purified by repeated treatment with hot dilute hydrochloric acid. It may be exposed in a closed crucible to a high temperature without undergoing alteration; it is not acted upon by acids or alkaline solutions, but if fused with hydrate of potassa it is converted into borate of potassa and ammonia. When heated to redness in a current of aqueous vapor, it is converted into boracic acid and ammonia.

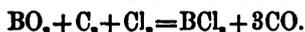
Nitride of boron is decomposed when heated together with easily reducible metallic oxides (*e. g.* the oxides of lead, copper, or mercury), binoxide of nitrogen being evolved.

BORON AND CHLORINE.

TERCHLORIDE OF BORON, BCl₃. *Sp. Gr.* 3.942.

Composition by Volume.—2 volumes of boron-vapor and 6 of chlorine condensed to 4 volumes.

This substance is obtained by passing dry chlorine over heated boron, or over an intimate mixture of boracic acid and charcoal, heated to redness in a porcelain tube. In the latter case it is mixed with carbonic oxide:—



It must be collected over mercury.

Properties.—The terchloride of boron is a colorless gas, producing white fumes when exposed to the air, in consequence of its immediate decomposition by moisture into hydrochloric and boracic acids. When passed through a very small quantity of water, it forms a solid hydrate.

BORON AND FLUORINE.

TERFLUORIDE OF BORON, BF₃. *Sp. Gr.* 2.31.

This compound, which is a colorless gas similar to the chloride, may be obtained by heating a mixture of 1 part of fused boracic acid, 2 parts of fluor-spar, and 12 of concentrated sulphuric acid.

Terfluoride of boron fumes when in contact with air, and has a powerfully suffocating odor. It chars organic substances rapidly; it may be condensed by intense cold to a clear colorless liquid. Water dissolves about 700 or 800 times its volume of this gas; a concentrated solution is best obtained by distilling together with concentrated sulphuric acid, a mixture of equal parts of fluor-spar and borax, previously fused together and powdered. The distillate is a very concentrated aqueous solution of the fluoride,¹ which is decomposed if diluted considerably, boracic acid being produced, together with *hydrofluoboracic acid*, which is probably analogous to hydrofluosilicic acid (§ 139), possessing therefore the formula, 3HF.2BF₃. Its formation would then be represented by the equation:—



¹ When water is completely saturated with terfluoride of boron, an acid is formed to which the name *fluoboracic acid* has been given; it is composed of boracic and hydrofluoric acids (3HF.BO₂), and its production may be explained by the equation:—



It may be prepared directly by dissolving boracic acid in hydrofluoric acid; it is a syrupy liquid, of sp. gr. 1.58, very acid, and capable of charring organic substances.

BORON AND SULPHUR.—When boron is heated to redness in vapor of sulphur, it burns a white or grayish substance being produced, which is *sulphide of boron*. This substance is rapidly decomposed by water, hydrosulphuric and boracic acids being produced.

SILICON (SILICIUM).

Sym. Si. Eq. 21.8.

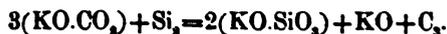
§ 136. Pure silicon was first obtained by Berzelius, in 1823. It is, next to oxygen, the most abundant substance in nature, but is only found in the form of teroxide, as silica, which occurs, not merely in the greater number of mineral substances (being almost the sole constituent of several, such as quartz and sandstone), but also in small quantities both in the vegetable and animal kingdom.

Preparation.—Silicon is obtained in a similar manner to boron, by heating the double fluoride of potassium and silicon with sufficient potassium to combine with the whole of the fluorine, according to the method given at § 134, and afterwards washing the mass with cold water, until no alkaline reaction is observable, then boiling with water to decompose any of the double fluoride which may not have been acted upon, and, finally, washing the silicon perfectly with hot water. Care must be taken not to employ too much potassium, since, in that case, a silicide of that metal is produced, which, when acted upon by water, is decomposed into silicon and potassa, with evolution of hydrogen (a portion of the latter being absorbed by the silicon, from which it may again be separated by a dull red heat); the alkaline solution which would thus be produced has a solvent action upon the silicon, more particularly if warm water be employed; the silicon then becomes converted into silica, hence the necessity of first washing with cold water.

Silicon may also be obtained by passing the vapor of chloride or fluoride of silicon over heated potassium, and afterwards washing the mass with cold water; or by heating silica with potassium; in the latter case, however, a considerable amount of silicide of potassium is produced, and the large quantity of potassa, resulting on the subsequent treatment with water, dissolves the greater part of the silicon, whereby it is reconverted into silica.

Properties.—Silicon, when pure, is a dark brown powder, heavier than water, devoid of lustre, which stains the fingers, and is infusible before the blowpipe; it is non-volatile; it increases in density when powerfully ignited, and assumes a chocolate tint; it appears to be thus converted into an allotropic modification, differing considerably in several of its properties from the silicon as it is originally obtained. The latter burns with a bright flame when moderately heated in oxygen or air, being partially converted into silicic acid; it unites with sulphur by the aid of heat, and is volatilized when heated with hydrofluoric acid. The chocolate modification may be heated to whiteness without burning, is not acted upon by hydrofluoric acid, and does not unite with sulphur. Berzelius concludes that the silicon contained in quartz, and all insoluble varieties of silica, is the allotropic modification, while the element exists in its original physical condition in soluble compounds of silicon.

When fused with dry carbonate of potassa, both modifications of this element are completely converted into silicic acid, the carbonic acid being decomposed, and carbon separated:—



Silicon forms only one compound with oxygen, silicic acid, or silica SiO_2 ; it unites with hydrogen, chlorine, bromine, fluorine, and sulphur, and enters also into direct combination with potassium, producing a silicide in the manner already described.

This element, like boron, exhibits a great similarity to carbon.

SILICON AND OXYGEN.

SILICIC ACID, SILICA, SiO_2 . *Eq.* 45.3. *Sp. Gr.* 2.66.

§ 137. This substance is found in nature perfectly pure, or very nearly so, as rock-crystal, quartz, flint, sand, chalcedony, opal, tripoli, agate, jasper, &c., and is an important constituent of a very large class of minerals.¹

It may be obtained by fusing 1 part of finely-powdered quartz or sand in a platinum crucible, with 2.5 parts of a mixture of equivalent weights of the carbonates of potassa and of soda, the mineral being added to the fused mass from time to time, in small quantities, as long as effervescence is observed. The fused substance, when cold, is dissolved in very dilute hydrochloric acid, the liquid separated by filtration from any insoluble portions, and evaporated to perfect dryness; the residue is once more heated with hydrochloric acid, it is then thrown upon a filter, washed with hot water, and afterwards dried and ignited.

Silica may also be obtained, in a state of very minute division, by passing the tetrafluoride of silicon into water, when hydrofluosilicic acid is simultaneously produced (§ 139). It may be prepared sufficiently pure, for many purposes, by igniting colorless rock-crystal, and immersing it while hot in water; after this treatment, the mineral may easily be pulverized.

Artificially crystallized silicic acid may be obtained by dissolving the silicate of copper, obtained by adding silicate of potassa to chloride of copper, in hydrochloric acid, precipitating the copper by hydrosulphuric acid, and evaporating *in vacuo* the filtered solution of silica in hydrochloric acid. White transparent needles of hydrate of silica are thus obtained, together with amorphous silica.

Properties.—Silicic acid, in the naturally crystallized state, is found as *rock-crystal*, in the form of six-sided prisms, terminated by six-sided pyramids, and is possessed of great hardness, though considerably inferior in this point to diamond or topaz. In the amorphous state, it occurs pure as *opal* (which contains in addition only a small quantity of water).

In the finely-divided state, as obtained by the above-mentioned process, it is a white powder, tasteless, but gritty. If strongly heated, it becomes very mobile and light, being easily dispersable by a slight current of air. It does not fuse at any furnace temperature, but may be liquefied by the flame of the oxyhydrogen blowpipe, or of a spirit-lamp, into which is forced a jet of oxygen, and also by means of a powerful voltaic battery. A clear glass is then obtained.

When silicic acid is precipitated from its combination with an alkali, by gradual addition of an acid, it assumes a gelatinous form (being then a hydrate), but passes over, when dried, into the pulverulent state.

When once separated from its solutions, silicic acid is not dissolved to any

¹ Way has lately discovered, at Farnham, large deposits of silica, in the condition in which it is readily soluble in hot solutions of caustic potassa or soda. These beds are situated at the base of the chalk formation, between the upper green sand and the gault clay. The discoverer proposes to employ these beds as a convenient source of silicate of lime for agricultural purposes. He finds that a mixture of slaked lime with the powdered rock, when made into a thin paste and left for several weeks, is entirely converted into silicate of lime. The action is promoted by the presence of 2 or 3 per cent. of carbonate of soda, the latter appearing to act as a carrier between the silica and the lime. Similar deposits had been previously found by Sauvage in the Département des Ardennes.

extent either by water or acids (with the exception of hydrofluoric acid); but if a large excess of concentrated hydrochloric, nitric, or sulphuric acid be at once added to the solution of an alkaline silicate, the silicic acid is completely held in solution, appearing to combine chemically with the acid at the moment of liberation. The silicic acid may be precipitated from solutions of this description by the gradual addition of an alkali, or of carbonate of ammonia.

The gelatinous silicic acid obtained by the decomposition of fluoride of silicon by water, is considerably soluble in the latter, yielding a tasteless solution, which possesses no acid reaction, and deposits the silicic acid, upon evaporation, as a white amorphous powder, soluble again in water. Addition of hydrochloric acid to the solution renders the silicic acid insoluble.

All waters are found to contain a larger or smaller proportion of silicic acid, which is deposited upon evaporation. In some waters it exists in combination with alkaline bases. Deposits of silica are formed from the waters of several hot springs, such as the *Geysers*.

A gelatinous *hydrate of silica*, of the formula $\text{SiO}_2 \cdot \text{HO}$, which has already been mentioned, is produced by gradually adding chloride of ammonium, or a mineral acid, to a solution of silicate of potassa, or by precipitating a solution of silica in an acid by an alkali or its carbonate; or, finally, by slowly and partially evaporating the solution of silica in hydrochloric acid.¹ It is purified by washing with hydrochloric acid and water. If allowed to dry in air, at ordinary temperatures, it gradually loses its gelatinous appearance, and forms a mass like gum, which finally passes over to a white powder. When this hydrate is heated to 212° F. (100° C.), it parts with one-half of its water, yielding a second hydrate of the composition $2\text{SiO}_2 \cdot \text{HO}$.

By exposing silicic ether to the action of moist air, Ebelmen has obtained hard transparent masses of hydrated silicic acid, similar in appearance to rock-crystal, and having the composition $2\text{SiO}_2 \cdot 3\text{HO}$.

Silicic acid is capable of displacing carbonic acid from its combinations at an elevated temperature. When fused with an alkaline carbonate before the blow-pipe, it forms a clear glass, the carbonic acid escaping with effervescence.² Sulphates even are decomposed by silicic acid at a high temperature, especially if carbon be present, which then exerts a reducing action upon sulphuric acid, converting it into sulphurous acid, which is of course far more readily expelled.

Silicic acid forms, with the more powerful bases, a class of salts termed *silicates*; they are generally produced by fusing silicic acid with the bases. The proportions in which this acid unites with bases are unusually various; it also forms numerous double-salts, those of the silicate of alumina with other silicates being the most abundant. The silicates in which the acid predominates are insoluble in water, and constitute the different varieties of *glass*, to be presently described.

It seems probable, from the remarkable difference in the properties of ignited and unignited silicic acid, that these are allotropic modifications of the same substance, and that each modification has its own particular class of salts.

The silicates are decomposed the more readily by strong acids, the more powerful the base, the less silicic acid, and the more water they contain. All silicates are gradually decomposed by digestion with sulphuric acid; after fusion with a carbonate of an alkali or an alkaline earth, they are also soluble in hydrochloric acid.

¹ If this evaporation be conducted *in vacuo*, crystals of silicic acid are obtained, as already mentioned.

² Finely-powdered silica has been found to decompose alkaline carbonates and bicarbonates, even when boiled for some time with their solutions. The carbonates of lime (prot-) oxide of iron and magnesia, appear also to be decomposed by silica under similar circumstances.

Those mineral silicates which are decomposed by the action of hydrochloric acid are termed *zeolitic*.

Uses of Silicic Acid.—This substance, more particularly in combination with alkalis or earths (*e. g.* in the form of *slags*), is extensively used in metallurgic operations, as a flux, for effecting the decomposition of metallic compounds by the solution of certain of their constituents, or for promoting the fusion of the slag, and thus aiding the separation of the metal.

It receives its most extensive application, however, in the manufacture of glass, porcelain, and earthenware; the two latter will be treated of under the head of alumina, § 211; we shall therefore confine ourselves at present to a brief consideration of the nature and properties of glass, its composition, and different varieties.

GLASS.¹

§ 138. This substance, so invaluable in all departments of science, arts, and manufactures, is a combination of two or more silicates, one of which is a silicate of an alkali, while the other may be either silicate of lime, baryta, oxide of lead, or (prot-) oxide of iron.

Glass differs from most natural silicates in being perfectly amorphous; it is produced by the fusion, at a more or less elevated temperature, of silicic acid together with various metallic oxides, such as potassa, soda, magnesia, lime, baryta, the (prot-) oxides of iron and manganese, the sesquioxides of iron and aluminum, the binoxides of manganese and tin, &c. The fused substance, being allowed to cool, solidifies to a transparent, amorphous mass, either colorless or not, according to the metallic oxides employed. The high temperature, assisting the comparatively weak affinities of silicic acid, induces it to unite with the bases, producing silicates of various composition.

Glass is possessed of high elasticity, considerable hardness and brittleness, and the power of resisting the action of the air and most other gases, and, to a great extent, that of water and a large number of powerful chemical agents.² In addition to these general properties, the various kinds of glass possess certain special characters, varying of course with their composition and the nature of the base they contain: it will therefore be advisable to take a brief survey of the special properties of the various silicates employed in the manufacture of glass.

The alkaline silicates, although the most fusible, vary considerably in this respect, according to the amount of base they contain. A mixture of $\frac{1}{3}$ of silicic acid with 2 or 3 times its weight of alkali, will fuse at a red heat, yielding a product easily soluble in cold water. As the proportion of silica increases, the fusibility of the product diminishes, as does likewise its solubility in water; those richest in silica are indeed scarcely attacked by the most powerful acids. Some

¹ We have to acknowledge the assistance afforded to us by Knapp's Technology, in writing the following history of glass.

² It has not yet been found possible to prepare a glass, however carefully, that is capable of withstanding perfectly the action of various agents, even of water. The liquid obtained by digesting powdered window or tube glass with a little water, has been found to be alkaline, and to contain silica. Glass vessels, and the glazings of porcelain or earthenware dishes, are all more or less attacked, if retained for some time in contact with boiling water. Glass that is exposed to the continued action of weather for a number of years, becomes more or less corroded. Acids will extract the bases from glass, separating the silica, and alkaline solutions will dissolve the silica, or at any rate loosen it, from the surface of the glass, to a considerable extent. Lead-glass is easily blackened if exposed to the action of sulphuretted hydrogen or soluble sulphides, and, if heated in a flame rich in carbon, is at once blackened, the lead being reduced by the action of the latter. Glass is most powerfully attacked by hydrofluoric acid, which acts both upon the silica and the bases.

of the alkaline silicates possess the property of cooling, after fusion, to a perfectly amorphous mass, passing over gradually from the liquid, through an intermediate pasty state, to solidification. This property is retained by them even when they are mixed with other silicates which crystallize; nay more, they exert an influence over these, preventing their crystallization, and thus rendering them manageable in the hands of the glassblower.¹

The silicates of the alkaline earths fuse only at a very high temperature. The silicates of lime and magnesia which correspond about to the formula $MO.SiO_2$ are the most fusible, requiring, however, the highest heat of a blast-furnace. The silicate of lime of that composition assumes a crystalline structure as it cools. The silicates of alumina are still more infusible; that corresponding to the formula $Al_2O_3.3SiO_2$, which appears the most fusible, cannot be liquefied in a blast-furnace.² The silicates of iron and manganese are far more easily fusible, but become crystalline on cooling; the silicates of lead are the more readily fusible, in proportion to the amount of oxide of lead they contain.

With regard to the silicates obtained in the manufacture of glass, it is difficult to say whether they are really in chemical combination; thus much is certain, that the properties of different simple silicates undergo considerable modifications when mixtures are made; thus, we have already stated that the presence of alkaline silicates will prevent the silicates of iron and manganese from assuming a crystalline structure; again, it is found that the temperature at which a complex silicate fuses is always below the mean of the fusing point of its component silicates; indeed, sometimes even below that of the most fusible of the silicates present.

The choice of bases, as also the proportions, employed in the manufacture of glass, must of course be regulated by the application which the product is to receive. The effect produced upon the nature of glass by the different metallic oxides already mentioned may be briefly stated to be as follows:—

Potassa and *soda* render the glass easily fusible; the *soda* adding to its brilliancy, but imparting to it a greenish tint; *potassa* does not tint the glass, but yields a somewhat less brilliant product.

Lime does not affect the color of the glass, but adds to its lustre, and also increases its hardness, while it decreases its fusibility. *Alumina* diminishes the fusibility of glass more than any other metallic oxide, while, on the other hand, *oxide of lead* renders it easily fusible, and also imparts to it a great degree of softness and brilliancy. Lead glass is also the most colorless, and possesses the

¹ It may be mentioned under this head, that the so-called *soluble glass* is an alkaline silicate, and is prepared by fusing together, in an earthen crucible, 15 parts of sand, 10 parts of pearl-ashes (crude carbonate of potassa), and 1 part of charcoal. The charcoal aids the production of the silicate, by the conversion of the carbonic acid into carbonic oxide, which escapes more readily, and also by the reduction of sulphuric acid, which is present in pearl-ashes. Cold water does not dissolve the resulting mass, it only removes any foreign alkaline salts that may be present. Upon boiling the silicate thus purified with 5 parts of water, it gradually dissolves completely: the solution may be concentrated to a syrupy, sticky liquid which gelatinizes on cooling, and on exposure to air becomes a transparent, colorless, brittle, but not very hard glass, possessing an alkaline reaction; it is itself unalterable by exposure to air, but becomes coated with a film of alkaline salt (carbonate), which may be removed by cold water.

This substance has been applied for diminishing the combustibility of wood, stuffs, paper, &c., by coating such substances with it, whereby they become protected from air. It may also be employed as an excellent cement for glass and porcelain, and finally for silicifying objects made of chalk and gypsum, by impregnating them with a solution of the glass, and afterwards exposing them to the air. A considerable degree of hardness may thus be imparted to such objects: they are even thereby rendered susceptible of a high polish.

² The only means by which these refractory silicates may be perfectly fused, is by the flame of the oxy-hydrogen blow-pipe.

highest refractive power. The action of *baryta* is similar to that of lead. The fusibility of glass is also increased by *iron* and *manganese*, but iron is liable to color the glass, particularly if it is present as protoxide, the green color thereby produced being more intense than the brown color afforded by an equal quantity of sesquioxide. Hence, glass which has a green tint, from the presence of protoxide of iron, may be almost decolorized by oxidation. A small quantity of binoxide of manganese, when added to a glass containing protoxide of iron, destroys the green color imparted by the latter, whilst the protoxide of manganese produced does not impart any color to the glass; if more binoxide of manganese be used than is necessary to oxidize the protoxide of iron, an amethyst color is imparted to the glass.

Various other metallic oxides are frequently used in the manufacture of glass, not so much to alter its nature as to impart to it various tints; we shall presently return to a brief consideration of these. It is found, in accordance with the above observations, that those kinds of glass which possess a high specific gravity (from 2.8 to 3.6, in consequence of the great density of the silicates they contain) are the softest, and also possess the greatest brilliancy and refractive power, while those varieties that are far less fusible, possess less brilliancy and a lower specific gravity (2.37 to 2.6).

It appears that the composition of a glass is not only dependent upon the proportion of the ingredients mixed together, but upon the temperature employed; the tendency possessed by silicic acid to unite in large proportions with bases being somewhat counteracted by the difficult fusibility of high silicates. A very high temperature tends also to volatilize portions of the alkaline bases from glass; thus complex silicates are found to decrease gradually in fusibility by continued exposure to a high temperature; this is not only owing to the volatilization of the alkalies, but also to the extraction of alumina from the glass-pots by the silica liberated. Excess of base in glass is equally prone to act upon the pots in the opposite manner, extracting the silica.

We have already stated that glass (in the extended sense of the word) is amorphous; when in its most liquid state (at the highest heat of the furnace) it is of the consistence of thin syrup, and may, when in that state, be cast into moulds or sheets. As the temperature cools down to a bright red heat, the glass becomes very tough and tenacious, and may, when in that state, be blown into any form, or drawn out into threads.

If a mass of glass be allowed to cool in the air, the outer portion solidifies first, and forms a coating which resists any change of position that might otherwise be assumed by the interior particles in the act of cooling; hence these latter exert a certain degree of tension upon the external layer of glass, and a slight concussion of the latter, insufficient of itself to destroy its continuity, will determine the rupture of the mass.¹ In order to avoid this inconvenience, glass vessels are generally *annealed* by slow cooling in ovens, the temperature of which is very gradually diminished; here the whole mass of glass solidifies almost simultaneously, and a state of permanent equilibrium is established among the particles.

The *devitrification* of glass, which is observed in masses which are exposed for a length of time to a temperature approaching to fusion, depends mainly upon the volatilization of alkali, but partly, also, upon a molecular change in the structure of the glass, resulting in a crystalline arrangement of the particles. *Réaumur's porcelain*, as perfectly devitrified glass has been termed, possesses a remarkable opacity and hardness, striking fire with steel.

¹ If a drop of melted glass is allowed to fall into cold water, it assumes an elongated form, terminating in a point, as is well known in the case of the *Rupert's drop*. If the thin extremity be broken, the tension existing between the particles will be immediately exerted, and the whole drop will fall to powder.

Having briefly noticed the general nature and properties of glass, we shall confine ourselves to an account of the materials employed by the glass-maker, and of the composition of the principal varieties of glass, referring the reader to special works on the subject for the practical details of glass-making.

Sand is the most general source of silica, since it requires less preparation than other varieties of silicious minerals. Ordinary sands generally contain iron, lime, and clay, and sometimes organic matter. The clay is removed by levigation, the lime is harmless, but the iron is objectionable in most cases; though easily removed by hydrochloric acid, the expense is, in many instances, too great; hence, sand free from iron, such as is found at Alum Bay (in the Isle of Wight), in Norfolk, Lancashire, Sydney, and New Holland, is always preferred.

The sand is generally heated in reverberatory furnaces before use, to expel organic matter, and to reduce it to a fine state of division.

Rock-crystal, *massive quartz*, and *flint*, are used for some kinds of glass; the fragments are heated to redness, and then thrown into water, when they may be very easily reduced to powder.

The *potassa* used is either common *ashes* or *crude potashes*, according to the quality of the glass. For *soda*, *barilla* or *soda-ash* is generally employed; soap-boilers' waste is also used for common kinds of glass; the sulphates of soda and potassa may likewise be advantageously employed, the sulphuric acid being reduced by means of a little carbon, and thus more readily expelled by the silica.

The *lime* may be furnished by limestone of any description, if not too poor, or too rich in alumina and magnesia. An excess of lime in the manufacture of glass is avoided, since it extracts the silica from the pots, thus speedily destroying them. *Lead-glass* is made from *litharge* or *red-lead*, the latter being preferred, since it is in a finer state of division, and furnishes available oxygen for the oxidation of impurities. As these oxides, in the commercial state, both contain iron and copper, red-lead is generally purified for glass-making. Too much lead is also injurious to glass, rendering it too soft, and coloring it yellow. When lead is employed, potassa is used exclusively as alkali, since soda imparts a bluish tint to lead-glass.

When *baryta* is required (as in bottle-glass, to increase its fusibility), *heavy spar* (sulphate of baryta) is added.

Some silicious minerals, which are more or less easily fusible, are used at times in the manufacture of glass. The principal are *basalt*, *clinkstone*, *loam*, *marl*, *pumice-stone*, &c. Some may be used alone as glass, such as basalt; others require the addition of lime or alkali to increase their fusibility.

The presence of impurities in some of the materials employed in glass-making, and which frequently impart a color to the product, renders the use of *decolorizing* agents necessary at times. The principal substances used are, *binaride of manganese*, *arsenious acid*, and *sulphuretted alkali*, all of which effect the oxidation of the impurities (such as carbon or iron).

Finally, *broken glass* (*cullet*) is always ground up and mixed with the materials for glass of a similar kind, before their introduction into the pots, the fusion of the mass being much assisted by its presence.

The production and fusion of glass is effected in reverberatory furnaces of various kinds, by hot flame-fires (the fuel employed is coal, or baked wood). The glass, or *metal*, as it is termed, is fused in large crucibles, or *pots*, of very refractory fire-clay, which have been very carefully annealed before use.

The different varieties of glass may be divided into two classes: first, those which consist mainly of silica, lime, and alkali, of which the principal are *crown-glass*, *window-glass*, the various kinds of *lucifer-glass*, and *plate-glass*; the second

¹ *Bohemian glass*, which belongs to this class, and is indispensable to the chemist on account of its efficient fusibility and power of resisting sudden changes of temperature, owes its properties especially to the circumstance of its containing only silica, potassa, and lime.

class comprises those glasses of which lead is an important ingredient, of these the principal are *flint-glass*, of which a kind is especially manufactured for optical purposes; *strass* or *glass-paste*, used for artificial gems, and *glass-enamel*.

The following tables exhibit the percentage composition of the principal kinds of glass, as determined from the analyses of various specimens:—

FIRST CLASS.

	Crown glass.	Window glass.	Bohemian glass. ¹	Plate glass.	BOTTLE GLASS	
					ordinary.	medicinal.
Silicic acid	62.8	69.1	76	74.4	58.4	66.4
Potassa	22.1	...	15	} 17.2	8.7	12.1
Soda	18.8	...			
Lime	12.5	12.9	8	5.4	22.4	18.7
Magnesia	2.8
Protoxide of manganese	0.8	1.5
Alumina	2.6	4.5	1	2.9	7.8	8.8
Sesquioxide of iron	1.4	4.4	...
Protoxide of lead	1.5

SECOND CLASS.

	Flint glass, or crystal.	Strass, or paste.	Enamel.
Silicic acid	54.9	38.5	31.6
Potassa	9.5	7.9	8.8
Protoxide of lead	35.1	58.0	50.3
Alumina	1.1	1.0	...
Sesquioxide of iron	0.6
Binoxide of tin	9.8

We have already referred to the property possessed by various metallic oxides, of imparting different colors to glass; the extensive application it has received from the earliest times in the production of colored or stained glass, painted glass, and glass-paste, renders an enumeration of the various coloring substances necessary.

Sesquioxide of iron, suboxide of copper, and gold (either in the state of purple of Cassius, perchloride of gold, or fulminating gold), are employed for obtaining a *red* color; the first of these three yields a *brownish-red* glass; the coloring power of the suboxide of copper is very intense, the smallest quantity rendering glass opaque; hence, in coloring glass with this oxide, the red glass is first prepared, and colorless glass coated with a thin layer of it (by what is termed *flashing*). The suboxide will readily seize oxygen during the fusion of the glass, producing the protoxide, which yields a green glass; hence reducing substances are generally added in fusions of this kind of glass.

Various shades of red, from *carmine* to *rose*, are obtained by the use of gold.

Yellow glass is obtained by means of glass of antimony, consisting of a mixture of tersulphide of antimony and antimonious acid, produced by incomplete roasting of the former. Antimoniate of potassa is also used. Charcoal is sometimes used for imparting a *brownish-yellow* tint (in some kinds of bottle-glass), the color being produced by the distribution of carbon in a fine state of division through

¹ The composition of Bohemian hard glass tubing (*combustion-tubing*), has been found by Rowney to be as follows:—

Silicic acid 78.18, lime 10.43, alumina 0.80, sesquioxide of iron 0.18, magnesia 0.26, protoxide of manganese 0.46, soda 8.07, potassa 11.49.

the mass. Chloride of silver yields a brilliant yellow with glass containing alumina. Sesquioxide of uranium is now extensively employed for coloring glass yellow; it yields a brilliant color, exhibiting a *greenish* tinge.

A *green* color is obtained, as already stated, by (prot-) oxide of iron, but the color obtained by means of oxide of copper is far more brilliant and beautiful; particularly if the glass to be colored contains lead. If the glass is dull or translucent, the color produced by oxide of copper is not green, but *blue*.

Sesquioxide of chromium yields the finest *green* color. Oxide of cobalt is the only substance used to impart a *blue* color to glass. The ores of cobalt contain a number of other substances (arsenic, sulphur, copper, nickel, iron, &c.), which it is necessary to remove as far as possible, since they exert great influence over the blue color yielded by the cobalt. The ores are levigated, roasted, and afterwards fused with proper proportions of finely-divided quartz and potashes. A deep blue glass is thus obtained, which, when ground and washed, receives the name of *cobalt smalts*, and is employed for coloring glass.

Other colors (called *mixed colors*) are imparted to glass by using mixtures of the substances just enumerated. Thus binoxide of manganese and smalt yield a *brown garnet* color; *orange* is obtained by the use of silver and iron; *flesh-color* by iron and alumina, &c.

These various colors are either introduced into the fused glass, or a colored glass is first prepared, with which the colorless glass is coated, or lastly, colored lead-glasses are prepared and finely ground as pigments, with which paintings are made on the glass, and afterwards burnt in.

In the manufacture of *artificial gems*, a very brilliant colorless flint-glass, containing a great quantity of lead, is prepared and carefully fused with the various colors employed. *Topaz* is obtained by the use of sesquioxide of iron, purple of Cassius, and glass of antimony; a *ruby* color is produced by purple of Cassius; *beryl*, by oxide of cobalt and glass of antimony; *garnet*, by purple of Cassius, antimony, and binoxide of manganese; *emerald*, by the oxides of copper and chromium, &c.

Enamel-glasses, employed extensively for coating vessels of various kinds, either for ornament or protection, consist of easily fusible lead-glass, which is either transparent or colored as above, or rendered opaque or milky, by the uniform dissemination, throughout its mass, of fine particles of some substance which cannot be fused at the temperature at which the glass is made. The substances generally employed for producing *opaque*, or *opalescent enamels*, are bone-earth, binoxide of tin, or teroxide of antimony.

Enamels may also be applied, like the colored glasses, as pigments, for which purpose they are reduced to a fine state of division, and are burnt on to the vessels, which are exposed to the necessary heat in muffles.

For the analysis of glass, see Quantitative Analysis, Special Methods.

§ 139. SILICON AND HYDROGEN.—In the description of the preparation of silicon, mention was made of the retention of hydrogen by that substance, obtained by the action of potassium on the fluoride, when it is washed with water. A chemical compound, the silicide of hydrogen, appears to be formed, which, when freed from silicic acid, by treatment with hydrofluoric acid, burns with brilliancy in oxygen or air, water being always produced. It parts with its hydrogen, yielding silicon, when very strongly heated in a covered crucible.

SILICON AND CHLORINE.—When heated in chlorine, silicon takes fire, forming tetrachloride of silicon, $SiCl_4$, as a vapor, which condenses, upon cooling, to a mobile liquid.

This compound may also be prepared by passing chlorine over an intimate mixture of charcoal and flint, strongly heated in a porcelain tube, or earthenware retort. It is purified from excess of chlorine by agitation with mercury, and distillation. It is then obtained as a transparent, colorless liquid, of

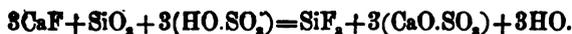
sp. gr. 1.52, which boils at 122° F. (50° C.), and does not solidify at -4° F. (-20° C.); it evaporates directly on exposure to air. Its vapor is suffocating, and is decomposed by moisture, forming dense clouds of hydrochloric acid, and depositing silicic acid. If the liquid is placed in contact with water, it is decomposed in a similar manner, the resulting silica remaining dissolved in hydrochloric acid.

SILICON AND BROMINE.—These elements unite to produce a compound similar in appearance and properties to tetrachloride of silicon, which is rapidly decomposed by water.

SILICON AND FLUORINE.

TERFLUORIDE OF SILICON, SiF_4 , is formed when hydrofluoric acid comes in contact with silicic acid, or a silicious substance, such as glass. The etching of glass by hydrofluoric acid (*see* § 102), is dependent upon the production of terfluoride of silicon.

This substance is prepared by heating in a glass or earthenware vessel, a mixture of equal parts of finely-powdered fluor-spar and glass, with 6 or 8 parts of concentrated sulphuric acid. In this reaction the oxygen in the silicic acid of the glass is replaced by the fluorine of the fluor-spar, according to the following equation:—

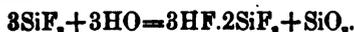


The sulphuric acid employed should be as strong as possible, and great care should be taken to have the apparatus perfectly dry, since the fluoride is easily decomposed by water. It must, therefore, be collected over mercury.

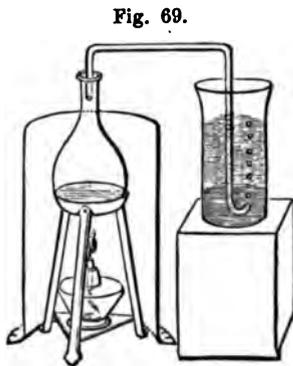
Properties.—Terfluoride of silicon is a colorless gas, of spec. grav. 3.6, which forms very dense fumes when in contact with a damp atmosphere.

When this gas is allowed to come in contact with water, it is at once partially decomposed, together with a certain quantity of the latter, silicic acid being separated, and hydrofluoric acid liberated, which immediately unites with a second portion of the terfluoride of silicon, producing a peculiar acid, termed hydrofluosilicic acid.

HYDROFLUOSILICIC ACID, $3\text{HF}.2\text{SiF}_4$.—The formation of this acid is shown by the following equation:—



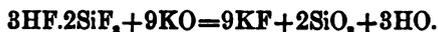
In order to obtain a solution of this acid, the fluoride of silicon obtained as above is transmitted into water; the mouth of the delivery-tube, however, must not be allowed to come in contact with the water, since it would very soon become choked up with the silicic acid liberated by the decomposition of the gas. A little mercury, or a small cup containing some of that metal (*Fig. 69*), is therefore placed at the bottom of the vessel of water, into which the extremity of the tube is allowed to dip. As each bubble of gas ascends through the mercury and enters the water, it becomes inclosed in a coating of gelatinous silicic acid, which rises to the surface, and then disperses as the gas is absorbed by the water; when the liquid through which the gas is passed is perfectly tranquil, tubes of the gelatinous silica are sometimes formed, through which the gas escapes undecomposed; it is necessary, therefore, to agitate



the liquid, from time to time, with a glass rod. When the water is saturated, it appears as a gelatinous, semi-transparent mass, owing to the quantity of the silicic acid separated. Upon the removal of the silica by filtration, a very acid liquid is obtained, which has the property of producing, in pretty concentrated neutral solutions of potassa, soda, and lithia, gelatinous, transparent precipitates; and in solutions of salts of baryta, a white precipitate, becoming crystalline after some time. Compounds resembling these in constitution, are formed with many metallic oxides when they are employed in sufficient quantity only to neutralize the hydrofluosilicic acid. It appears that, under these circumstances, the hydrogen in the acid is replaced by metal, double fluorides of the metal and of silicon being produced:—



The general formula of these salts, therefore, is $3\text{MF} \cdot 2\text{SiF}_3$. If the bases be added in excess, simple metallic fluorides are produced, together with silicic acid:—



Upon allowing a solution of hydrofluosilicic acid, containing the silica separated in its formation, to evaporate slowly in a warm place, the whole disappears after a time; the hydrofluoric acid, reacting upon the silicic acid, gives rise to the formation of fluoride of silicon. If a clear solution of hydrofluosilicic acid be allowed to evaporate in a glass or porcelain vessel, it will also become reconverted into fluoride of silicon, the silicic acid necessary to the reaction being supplied by the material of the vessel, which therefore becomes etched.

SILICON AND SULPHUR.—A combination of these substances may be produced by heating silicon in vapor of sulphur; the union is attended with evolution of heat and light. A white, earthy substance is obtained, which burns slowly when heated in air, yielding silicic and sulphurous acids; on exposure to moist air, at ordinary temperatures, it is gradually converted into silicic acid, hydrosulphuric acid being evolved.

A *chlorosulphide of silicon*, of the formula SiSCl_2 , has been obtained by passing the vapor of terchloride of silicon and dry hydrosulphuric acid together through a porcelain tube, heated to redness. It is a colorless liquid, evolving pungent fumes on exposure to air; it boils at about 212°F . (100°C .), and has a sp. gr. of 1.45. It is decomposed by water into hydrochloric, hydrosulphuric, and silicic acids, together with a small quantity of sulphur.

It appears that the second and third equivalents of chlorine in terchloride of silicon may also be replaced by sulphur. The existence of a compound of the formula, SiS_2Cl has not yet been properly established, but the *tersulphide of silicon* SiS_3 has been obtained pure. It is obtained as a residue when crude chlorosulphide of silicon is distilled.

THE METALS.

§ 140. In treating of the second class of elements, the metals, we shall divide these bodies into groups according to the deportment exhibited by them, or by their oxides, with particular reagents; this classification is the same as that employed in the analytical section, and is adopted in this place, in order that it may be impressed upon the memory of the student; since, however, this grouping of the metals is of far greater importance in analysis than in their general history, it is fully explained in the introduction to that branch of study, and thither we must now refer for further information, though, for our present purpose, it is really unnecessary, and indeed premature, to understand the principles of such a classification, the reader being called upon only to bear in mind that it exists.

We have already shown in what consists the difference between a metal and a non-metallic element, and will now merely recapitulate the chief points of dissimilarity.

A metal is a better conductor of heat and electricity than a non-metallic body.

Metals are capable of forming bases by combining with oxygen.

Generally speaking, metals have a greater affinity for non-metallic substances than these have for each other, and the result of the combination of a metal with a non-metallic body usually exhibits the properties of a salt.

The combinations of metals with each other are termed *alloys*, except when mercury enters into the compound, which is then known as an *amalgam*.

Were we to enter here into the general description of the relations of the metals to oxygen, sulphur, and other non-metallic bodies, we should only have to instance and describe examples which would be of necessity repeated in the history of the particular metals to which such examples belong, and hence we shall pass on at once to the special consideration of the metals.

METALS OF THE FIRST GROUP.

(Metals of the Alkalies.)

POTASSIUM.

Sym. K. Eq. 39. Sp. Gr. 0.865.

§ 141. Potassium was discovered by Sir H. Davy, in 1807. It occurs in nature always in combination; many minerals contain this metal; we may especially notice *felspar*, which is a double silicate of alumina and potassa ($\text{KO.SiO}_3.\text{Al}_2\text{O}_3.3\text{SiO}_2$). It is also found in sea-water and in most mineral waters, in soils, and hence also in plants, which contain potassa, sometimes as silicate, and more generally in the form of salts with organic acids, which upon incineration, furnish carbonic acid, with which the potassa is found in combination in the ashes of such plants; the ashes of land-plants are much richer in potassa than those of marine plants. Potassa is also found, in combination with nitric acid, forming nitre, or saltpetre, as an incrustation on the soil in certain hot climates.

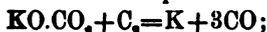
The chief source whence potassium itself is obtained is the bitartrate of potassa ($\text{KO.HO.C}_6\text{H}_4\text{O}_{10}$), which is known in commerce under the names of *argol* and *cream of tartar*, and is the salt deposited in large quantity during the fermentation of the grape-juice in the preparation of wines.

Preparation.—Potassium was originally prepared by its discoverer by subjecting one of the oxides, potassa, to the action of a powerful galvanic battery, the negative pole of which was in contact with mercury; the oxygen of the alkali was disengaged at the positive pole, and the metal at the negative pole, where it entered into combination with the mercury, forming an amalgam which was subjected to distillation, when the potassium was left behind in the retort. This metal may also be prepared in small quantity by passing hydrate of potassa, in a state of vapor, over iron heated to whiteness.

In practice, however, potassium is now always prepared by the deoxidation of potassa, by means of charcoal at a high temperature. In order to effect this, an intimate mixture of carbonate of potassa and charcoal is prepared by calcining the bitartrate of potassa in a covered crucible; when the salt $\text{KO.HO.C}_6\text{H}_4\text{O}_{10}$ is heated in close vessels, it evolves water, together with certain vapors resulting from the decomposition of the tartaric acid, whilst one part of the carbon remains behind, as carbonic acid, in combination with the potassa, and another part in the free state, mechanically mixed with the carbonate.

The mixture of carbonate of potassa and carbon thus obtained, is mixed with an additional quantity of ordinary wood-charcoal, and introduced into an iron mercury-bottle, covered with clay to enable it to resist the action of the fire; an iron tube is tightly screwed into the bottle, and communicates with a receiver of a particular construction, containing a quantity of petroleum in which the potassium is condensed, and provided with an exit-tube for the gas evolved; the iron

bottle is very strongly heated in a furnace with a good draught, when the potassium distils over into the receiver, which is kept cool by a stream of water. The action of the carbon upon the carbonate of potassa is very simple:—



but when the vapor of potassium and the carbonic oxide pass from the retort into the tube, in which they are subjected to a lower temperature, a decomposition of the carbonic oxide takes place, and a peculiar solid compound containing potassium is formed, which not only entails a considerable loss of this metal, but is very liable to stop up the tube, thus giving rise to the most dangerous explosions; hence it is necessary that this tube be unstopped from time to time; in fact, very many precautions are necessary in the preparation of potassium, and we have only given an outline of the process, as far as it possesses a general interest, referring to larger works for a more detailed description of the difficulties to be overcome in practice. In order to purify the potassium obtained in this process, it is fused under petroleum and strained through linen; it may then be redistilled in the vapor of petroleum, and preserved in small bottles filled with this liquid or with benzol.

Properties.—Potassium is a bluish-white lustrous metal, which oxidizes very rapidly when exposed to air, becoming converted into potassa, on which account it is always preserved, as above directed, in a liquid free from oxygen; it is brittle at low temperatures, but at the ordinary temperature may be cut like wax; it fuses at 25° C. (136°.4 F.), and may be distilled unchanged in an atmosphere free from oxygen, at a red heat; the vapor of potassium has a green color. The specific gravity of this metal being only 0.865, it floats upon the surface of water, which it decomposes even at the ordinary temperature, combining with the oxygen with such energy that the metal is raised to a temperature sufficiently high to kindle the liberated hydrogen, which burns with a violet flame, from the presence of a little vapor of potassium; after this experiment, the water will of course present an alkaline reaction, due to the potassa which it now holds in solution. When potassium is heated in air, it burns with a fine violet flame, being converted into potassa.¹

The powerful affinity for oxygen which potassium exhibits, renders it very useful in many operations; thus, it will be remembered that this metal is employed in the preparation of boron and silicon, and we shall hereafter have occasion to mention its use in reducing various metallic oxides. In experiments upon organic substances, potassium is also found useful for removing oxygen, chlorine, bromine, &c.

POTASSIUM AND OXYGEN.

Potassa KO.
 Teroxide of potassium KO₂.

§ 142. Berzelius believed that the gray substance produced when potassium is burnt in an insufficient supply of air, or when thin plates of the metal are exposed to a moist atmosphere, consists of a *suboxide of potassium*, K₂O. When placed in contact with water, it is converted into potassa, with disengagement of hydrogen, which does not inflame.

POTASSA, KO. Eq. 47.

Preparation.—Anhydrous potassa may be obtained by heating the hydrate

¹ The combustion, however, is never complete, since the metal becomes covered with a film of potassa, which protects it from further oxidation.

KO.HO with an equivalent weight of potassium, in an atmosphere free from oxygen; decomposition of the water then takes place, and two equivalents of potassa are produced; thus:—



Properties.—Anhydrous potassa is a hard gray solid, fusible at a little above a red heat, and convertible into vapor at a very high temperature. When this substance is added to an equivalent quantity of water, very energetic combination takes place, and so much heat is developed that the resulting hydrate of potassa fuses and becomes redhot. Since the anhydrous potassa has received no application, it need not further occupy our attention.

HYDRATE OF POTASSA, CAUSTIC POTASSA.

KO.HO. *Eq.* 56.

§ 143. This is a compound of very great importance, since it is constantly employed in chemical operations.

Preparation.—Hydrate of potassa is generally prepared from the carbonate. One part of carbonate of potassa is dissolved in ten parts of water, in a clean iron pan, and the solution raised to the boiling point; to this solution is now added, by small portions at a time, a quantity of milk of lime, prepared by slaking one part, at least, of good quicklime with warm water, in a covered pan; the mixture should be allowed to boil for a minute or two after each addition of lime, and the water which evaporates should be replaced; when all the lime has been added, a small portion of the liquid is removed from the pan, and allowed to stand till the lime has subsided; the clear liquid is then decanted, and mixed with excess of dilute hydrochloric acid; should any considerable effervescence be produced, fresh portions of milk of lime are added to the boiling liquid till this is no longer the case; the pan is then covered, and the mixture boiled for a quarter of an hour, after which it is removed from the fire, and allowed to stand until all the solid particles have subsided; the clear liquid may be drawn off with a siphon (those portions which are still turbid may be set aside in stoppered bottles of green glass), and rapidly evaporated, in a silver basin, either to the requisite state of concentration, or, if the solid hydrate be required, until the hydrate itself begins to pass off in white fumes, when it may be poured upon a clean iron plate, and allowed to cool. If a scum of carbonate of potassa be formed upon the surface of the fused hydrate, it should be removed before pouring the latter from the pan.

The decomposition is thus represented:—



In this process, simple though it appears, considerable care is required to insure a good result; thus, if too small a quantity of water be present, the carbonate of potassa will not be decomposed by the lime; in fact, a strong solution of potassa is capable of withdrawing the carbonic acid from carbonate of lime. Again, if the mixture be not boiled after each addition of milk of lime, the carbonate of lime will not subside readily, and the resulting solution of potassa will be turbid. It is important that the pan in which the potassa is prepared be made of untinned iron, or of silver, since tin and copper would be acted upon by the alkali; the vessel in which the solution is allowed to subside should be covered, for the potassa is very prone to be reconverted into carbonate by absorption of carbonic acid from the air. The solution of potassa should be preserved in stoppered bottles, the glass of which is free from oxide of lead, since this latter is soluble in potassa; bottles of German glass, or of common green glass, are the best.

The hydrate of potassa thus prepared is liable to contain various impurities,

derived from the lime and carbonate of potassa; these are particularly noticed, and the method of discovering them described, in the section upon reagents. A purer variety of hydrate of potassa, known as *alcohol-potash*, is prepared by agitating the syrupy hydrate with alcohol, decanting the alcoholic solution, and evaporating. Pure potassa is also prepared from carbonate of potassa obtained by incinerating well-washed bitartrate of potassa; the lime for this purpose is generally obtained by the calcination of oyster-shells in an open fire.¹

Properties.—Hydrate of potassa, when perfectly pure, is a white, hard solid (as met with in commerce, it is often in the form of thin sticks (*potassa fusa*), which have been cast in moulds, and have a bluish-green color, due to the presence of manganate of potassa). It fuses below a red heat, and at a higher temperature volatilizes in white vapors. The water cannot be expelled by heat. Placed in water, it dissolves rapidly, with disengagement of heat and a slight hissing sound. It also dissolves very readily in alcohol, which, after a short time, it decomposes, yielding a brown solution. When exposed to the air, it deliquesces to a syrupy liquid, which gradually absorbs carbonic acid, and passes into carbonate of potassa.

Hydrate of potassa is the most powerful alkali which we possess; its solution in water has a very soapy feeling on the skin, and immediately restores the blue color to reddened litmus, or imparts a brown color to turmeric. When brought in contact with acids, the water is displaced, and the potassa combines with the acid to form a potassa-salt. The salts formed by potassa with strong acids, when neutral in constitution, are also neutral in reaction. These salts are, with few exceptions, soluble in water.

The aqueous solution of potassa (*liquor potassæ*), which is so very useful both as a chemical and medicinal agent, is prepared by arresting the evaporation of the liquid obtained by decomposing the carbonate of potassa with lime, as soon as it has attained a certain strength; this is indicated by the specific gravity of the solution, the amount of hydrate of potassa in which increases with its density. By reference to the tables given in larger chemical works, we may ascertain the amount of potassa contained in solutions of various densities. The *liquor potassæ* used in medicine has a specific gravity of 1.06, and appears to contain about 5 per cent. of real alkali. The ordinary solution employed in the laboratory contains about 25 per cent., and has a specific gravity 1.27.

Solution of potassa boils at a higher temperature than water, and the stronger the solution the higher will be its boiling-point; this solution, and all other strong alkaline solutions, should never be heated in vessels of glass or porcelain, since they readily attack these materials. Solution of potassa attacks cork, and must therefore be preserved in stoppered bottles.

A solution of hydrate of potassa in a very small quantity of hot water, if allowed to cool in a stoppered bottle, deposits small rhombohedral crystals of the formula $KO+5HO$, which dissolve in water with production of cold. Potassa, as has been already mentioned, may be decomposed by a powerful galvanic current; certain metals, iron and zinc, for example, at a high temperature, are also capable of abstracting its oxygen. Hydrate of potassa, when fused with sawdust and many other organic matters, oxidizes them at the expense of the water which it contains, hydrogen being evolved, and the potassa remaining as carbonate, the carbonic acid being formed by the oxidation of the carbon of the organic matter. We have seen that potassa is reduced by carbon at a high temperature. If chlorine be passed over potassa at a red heat, it displaces the oxygen, chloride of potassium being formed; whilst, if chlorine be allowed to act upon a solution of potassa, we obtain chloride of potassium, and a salt of potassa with an oxygen-

¹ Pure potass is sometimes prepared by decomposing sulphate of potassa with hydrate of baryta.

acid of chlorine; the same is the case with bromine and iodine; an analogous reaction takes place between potassa and sulphur or phosphorus, a sulphide or phosphide of potassium being formed, together with a salt of potassa with one of the oxygen-acids of these elements.

Uses of Potassa.—The solid hydrate of potassa is extensively used by the chemist for drying gases, for decomposing mineral silicates and various organic substances. It is also applied in surgery as a caustic. Solution of hydrate of potassa is extensively used by the soap-maker for preparing soft soap, and is constantly employed in the laboratory, where its very powerful alkaline properties render it useful for displacing weaker bases, and for absorbing acid gases, for example, carbonic acid, in organic analysis. In medicine, the solution of sp. gr. 1.06 is administered as an antacid, and as a solvent of uric acid in cases of gravel, &c.

NITRATE OF POTASSA, NITRE, SALTPETRE. KO.NO_3 .

§ 144. This salt occurs in nature as an incrustation upon the surface of the earth in hot climates, such as India, Arabia, and South America. It is also found in certain caverns in Ceylon and other parts; these natural excavations occur in a limestone, which contains magnesia and feldspar. Some of these caves are the resort of innumerable bats, whose excrement collects in them, and doubtless is a great source for the production of nitre in these localities.

Saltpetre, as it is found in these crusts or deposits, is always more or less contaminated with the nitrates of lime, magnesia, and soda, besides their chlorides and sulphates.

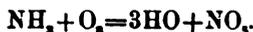
Nitrate of potassa is also found in small quantities in the juices of plants, and in some waters.

In some of those localities where nitre-incrustations are found, this salt appears to exist in small quantities in the soil, being collected upon its surface by the heat of the sun, which causes the superficial moisture to evaporate, and deposit the salt dissolved in it, while the crust of earth, thus becoming very dry and porous, draws up fresh quantities of moisture, containing nitrates, from beneath, which is in turn evaporated; in this manner the crust of salt deposited gradually increases in thickness.

In other localities, however (*e. g.* in some of the caverns above alluded to), the saltpetre is evidently formed gradually, by the decomposition of animal and vegetable matter, in contact with certain bases.

Many examples might be quoted of the production of nitrates in this manner; we may mention, as one, the production of the so-called *saltpetre-rot*, a plumose incrustation of nitrates which is frequently observed upon the base of the external walls of buildings in crowded cities, imperfectly drained, when nitrogenized organic matter (manure) mixes with earthy salts in the street, or attaches itself to the mortar of the buildings.¹

§ 145. It has already been stated that the production of nitric acid, from organized substances, appears to depend upon the oxidation of the ammonia produced in the putrefaction of nitrogenized bodies, at the expense of the atmosphere, in the presence of powerful bases, with which the nitric acid thus formed may combine; thus:—



The existence of the bases in a porous condition is believed to assist the formation of nitric acid, probably by the great condensing power which porous

¹ This species of incrustation must not be confounded with a similar efflorescence frequently observed on the walls of new buildings (particularly if these are plastered over), and which consists of sulphates and carbonates of the alkalis contained in the building materials, and gradually brought to the surface as the structure dries.

substances are known to exert over gases, thus bringing them within the sphere of action of chemical affinity.¹ This argument receives great support from the fact that ammonia may be converted into peroxide of nitrogen, by passing it over spongy platinum heated to 572° F. (300° C.) It is obvious that, if that oxide can be thus formed, there is no obstacle to its final conversion into nitric acid.

Artificial production of Nitrates.—In countries where nitre does not occur, or where it is not easily imported, large quantities are prepared artificially, by what is termed the process of *nitrification*, the conditions necessary for the formation of nitrates being carefully attended to.

Vegetable and animal refuse containing nitrogen, such as the sweepings of slaughter-houses, dung, weeds, &c., is made into heaps with earth, limestone, old mortar, and ashes; these heaps are sheltered from rain, and are moistened from time to time with urine; after several months, an incrustation of nitrates forms on the surface; when sufficiently rich (or *ripe*), the *nitrified earth*, as it is termed, is extracted in the manner to be presently described.²

In the Prussian saltpetre plantations, the nitre-beds are constructed in such a manner that they are never completely removed. That side of the mound which is exposed to the prevailing wind is perpendicular, while the back portion is built up in steps. The heap is watered from behind, while, as the front wall is exposed to the desiccating action of the wind and sun, the nitrates are there collected, and the rich outer coating is removed from time to time, fresh portions of material being added to the heap from behind.

In Sweden, where nitre is a revenue-tax, most of the peasants possess a nitre-plantation on a small scale. Heaps are constructed in sheds, of the materials enumerated above, watered from time to time with urine, and maintained in a porous condition by the insertion of twigs. The mass is turned occasionally, and allowed to remain generally about two years.

In other countries (*e.g.* in Switzerland, where the stables are erected against the sides of the mountains), the liquid manure that penetrates through the roughly boarded floors of the stables, is collected beneath, in pits filled with a mixture of the above-mentioned substances.

The time required for the production of nitrates, in any quantity, varies considerably with the temperature of the atmosphere. It has been observed that from 59° to 68° F. is the temperature most favorable to the production of nitrates, while their formation is completely checked at 32° F.

PREPARATION AND PURIFICATION OF NITRE.—The separation of the nitrates from the earth is effected by *lixiviation*. The nitrified earth is broken up into small lumps, and placed in large tubs or troughs with false perforated bottoms, and lateral openings below these, stopped with plugs until required. The perforated bottom is covered with a layer of straw or small twigs, to prevent the holes from becoming stopped up by portions of the earth. Sufficient water is added to cover the earth, and allowed to remain together with it for about twelve hours, in order that the salts may be thoroughly extracted. The solution or lye

¹ Some chemists imagine this power capable even of inducing the nitrogen and oxygen of the air to unite directly to form nitric acid, provided some impulse be imparted to their particles by the presence of organic matter undergoing decomposition, or of ready-formed ammonia. In support of their argument, they call attention to the large amount of animal matter required to produce any quantity of nitric acid, and to the circumstance that ammonia continually escapes into the atmosphere, whence it may be rapidly absorbed by porous earth or rocks, being one of those gases over which such bodies exert their influence in the most powerful manner.

² One thousand cubic inches of good nitrified earth yield about five ounces of saltpetre. The surface of the mounds upon which the nitrates collect is removed from time to time, and set aside for lixiviation. It is generally about three years before a large nitre-mound is completely removed.

is afterwards allowed to run off from the openings at the bottom of the vessel.¹ Generally, the liquor obtained from one quantity of earth is poured upon a second, and even a third, in order that a tolerably concentrated solution of nitrates may be obtained. This lye, which contains the nitric acid in combination with lime, magnesia, potassa, soda, and ammonia, besides considerable quantities of chlorides and sulphates of these bases, is now mixed with a strong solution of carbonate or sulphate of potassa, when the whole of the nitric acid is converted into nitrate of potassa.

The solution is allowed to stand until clear, when it is decanted, and transferred to a boiler, where it is rapidly boiled down until it has attained a certain strength. A large quantity of the impurities are separated in this operation; small quantities of earthy salts are first deposited, and as the solution becomes more concentrated, the chlorides of potassium and sodium (of which it contains very considerable quantities) separate in small crystals, the solubility of these salts in water being only slightly increased by heat, when compared with that of nitre under similar circumstances.² When the liquor has attained a certain specific gravity, it is drawn off from the boiler, and allowed to remain undisturbed, in large pans, at a temperature of about 122° F. (50° C.) until the chlorides have separated as far as possible; it is then decanted into other vessels, and allowed to crystallize.

The nitre thus obtained is still contaminated with small quantities of alkaline chlorides and with organic coloring matter. It is now digested with the smallest quantity of hot water necessary for the complete solution of the saltpetre (whereby a further quantity of chlorides is sometimes separated). The solution is then boiled with a small quantity of glue or gelatin, which possesses the property of rendering insoluble the whole of the organic matter by its coagulation, and collects as a scum upon the surface of the liquid, from which it is easily removed. When the solution is sufficiently concentrated, it is allowed to run through funnel-bags into crystallizing-pans, where it is continually agitated with wooden stirrers, until crystals are no longer deposited. The object of this may be explained in a few words: if a solution of nitre is allowed to crystallize undisturbed, it deposits very large striated crystals, containing considerable cavities, in which are inclosed portions of the mother liquor; if the latter contain any impurities, they will consequently be, to some extent, retained by the crystals. But if a solution of nitre, as it crystallizes, be continually stirred, the salt is deposited in very fine grains (called *saltpetre-flour*), which may be very easily freed from any trifling quantity of impurity that may adhere to their surfaces.

In order to avoid loss of product by washing this saltpetre-flour with water (which must, of course, dissolve a considerable quantity), recourse is had to a very ingenious method of purification, dependent upon the power possessed by water of exerting its solvent action upon several salts simultaneously, the amount of one salt present in a quantity of water not preventing the solubility of another, or of a third salt, in the same water.

The saltpetre-flour is placed in a trough, similar to that employed in the process of lixiviation; a saturated solution of pure nitre is then poured upon it, and allowed to remain in contact with it for a short time. Any chlorides that may

¹ The lixiviated earth still retains a small quantity of nitrates, and is used, in the saltpetre plantations, for the construction of fresh mounds.

² The solubility of nitre at 212° F. (100° C.) is about 14 times greater than it is at ordinary temperatures, while that of chloride of potassium is only about twice as great, and that of chloride of sodium is but slightly increased. If, therefore, a solution containing these three salts be concentrated, the greater quantities of the chlorides will be deposited as the water decreases, while the nitrate of potassa will not exhibit any symptom of crystallizing out.

The crystals of chlorides deposited in the above process are allowed to collect in a *small basket suspended in the lye.*

still have been retained by the saltpetre are dissolved in this way, without loss of nitro. The solution is afterwards drained off, and the washing repeated twice or three times, when the nitre is obtained absolutely free from chlorides. The solution of nitre is afterwards employed for the first washing of a fresh portion of saltpetre-flour. The latter is then dried at a moderate temperature.

At Waltham Abbey, the refining of saltpetre is effected in a somewhat different manner. It is decolorized by boiling its solution with freshly-ignited charcoal, and is afterwards freed perfectly from chlorides by repeated recrystallization.

§ 146. *Properties of Nitre.*—Nitrate of potassa is a dimorphous salt,¹ crystallising in colorless, six-sided prisms, and in flattened rhombohedra, neither of which contains any water of crystallization; its specific gravity is 1.933. When heated, the crystals of nitre first decrepitate, from the expansion of water mechanically inclosed by them; at a higher temperature, about 662° F. (350° C.), they fuse, and are ultimately decomposed, yielding, at first, oxygen, the residue consisting of nitrite of potassa (KO.NO_2); if this be further heated, nitrogen and oxygen are evolved, and a mixture of potassa and peroxide of potassium (KO_2) remains.

Fused nitrate of potassa is translucent, and possesses a fibrous, crystalline structure; it is known in pharmacy by the name of *sal prunelle*.

Nitrate of potassa has a saline, cooling taste; it dissolves in about 5 parts of cold water (causing considerable depression of temperature), and in less than its own weight of boiling water. Nitrate of potassa is very slightly soluble in alcohol.

This salt acts, at high temperatures, as a very powerful oxidizing agent; thus sulphur and carbon, when dropped into fused nitre of a pretty high temperature, are oxidized with great violence, sulphate and carbonate of potassa being formed; in these and similar cases, the nitrogen is either evolved in the free state, or as an inferior oxide. Even silver, gold, and platinum, cannot resist the oxidizing action of nitrate of potassa.

§ 147. *Uses of Nitre.*—This salt receives its most important application in the manufacture of gunpowder,² and in pyrotechny; it is also used for some kinds of instantaneous matches.

The powerfully oxidizing properties of nitre have been applied from a very early period for the preparation of explosive mixtures. Besides gunpowder, the period of the discovery of which cannot be satisfactorily traced, we may mention a mixture possessed of powerfully explosive properties, known by the name of *pulvis fulminans*, which consists of 3 parts of nitre, 2 parts of dry carbonate of potassa, and 1 part of sulphur. This mixture explodes powerfully, when dry, if heated upon an iron plate.

Saltpetre is also used for the preservation of meat. It is sometimes employed for the manufacture of nitric acid, and is of great value to the chemist as a powerful oxidizing agent. In medicine, nitre is also extensively used.

Baumé's flux consists of 3 parts of nitre, 1 part of sulphur, and 1 part of sand; it is capable of inducing the fusion of different metals, partly on account of the heat evolved by its deflagration, and partly because it converts a portion of the metal into a more fusible sulphide.

¹ The dimorphism exhibited by nitre is similar to that of carbonate of lime; the prismatic crystals being very nearly the same as those of arragonite, while the rhombohedra are almost identical with those of calcareous spar.

² Nitrate of potassa, when pure, does not attract any moisture from the air; it is in consequence of this absence of deliquescent properties, and the comparative facility with which it may be purified from deliquescent salts, that it is employed in the manufacture of gunpowder, in preference to nitrate of soda, which occurs in much greater abundance, but is a very deliquescent salt.

EXAMINATION OF NITRE.

§ 148. It is of great importance to possess some good means of ascertaining the value of samples of nitre. The following are the principal methods employed for this purpose.

The most simple of these, and the one that is most extensively employed for the rough estimation of the value of nitre, is that of examining the *fracture* of the fused salt.

It has been mentioned that fused nitre possesses a peculiar fibrous structure; the presence of foreign salts affects this structure to a greater or less degree, according to their quantity. A slight percentage of chloride of sodium, for example, gives rise to small nodules in the mass; in long-practised hands, the percentage of nitre can be ascertained, by this physical examination, with sufficient accuracy for mercantile purposes; no reliance can, however, be placed in it by a casual experimenter. A cube of nitre, of 1 or 2 inches in thickness, is cast in an iron mould; it is afterwards broken in halves, and the fracture examined.

The examination of nitre by this method is called the *refraction of nitre*, which name is also applied in general to the examination of nitre by any of the processes in common use.

There are two other physical methods of examining nitre; one of these consists in washing a known weight of the dried salt with a saturated solution of pure nitre, upon a filter of known weight, until no reaction is obtained with nitrate of silver in the washings; afterwards carefully spreading the filter open upon a porous tile, in order that as much as possible may be absorbed of the solution that is mechanically retained, and finally drying in the water-bath. The loss in weight which the nitre and filter will have sustained, indicates the amount of impurities in the nitre. This method is tedious, and always yields results from 1 to 2 per cent. too high, in consequence of the addition to the substance operated upon, of a small quantity of nitre, left by evaporation of that portion of the solution which is inevitably retained by the surfaces of the crystals, and by the filter. The error may be, to a great extent, corrected by weighing the filter and contents, before and after desiccation, and deducting from the second weight the amount of nitre known to correspond to the quantity of water evaporated.

Another source of error arises from the increased solubility of nitre in a solution containing chloride of sodium, in consequence of the mutual decomposition of these salts giving rise to chloride of potassium, and nitrate of soda; tables have been constructed, from direct experiments, to enable the analyst to make the requisite correction.

The second physical method is based upon the principle that the solution of a crystallizable salt in a certain amount of hot water, upon being allowed to cool down, first commences to deposit crystals at a temperature standing in direct relation to the amount of salt dissolved; and that this temperature is the same, whether the solution contain other salts in addition or not.

A scale is first constructed of temperatures at which cooling solutions of nitre of different strength commence to crystallize, a fixed amount of water (100 parts) being taken in each observation. A known weight of the sample to be examined is dissolved in a beaker, at about 140° F. (60° C.), in the same amount of water as that employed in constructing the table; a thermometer indicating $\frac{1}{4}$ ° is then introduced, and the temperature noted at which the first symptom of crystallization is perceptible. By simple comparison of this temperature with the table, the amount of nitre in the solution is at once ascertained.

An inaccuracy in this determination may arise from the presence of chloride of sodium, which would tend to depress the temperature of the crystallizing-

point, by decomposing a certain quantity of the nitre in the manner above alluded to.

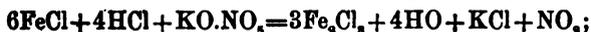
Gay-Lussac's method of examining nitre consists in mixing about 20 grains (accurately weighed) of the dried specimen, with about 10 grains of charcoal-powder and 80 grains of chloride of sodium; this mixture is introduced by small portions into an iron crucible heated to redness; the fused mass is dissolved in water, the solution colored with litmus, and dilute sulphuric acid of known strength added from a graduated glass until a slight excess has been employed, which is known by the peculiar bright-red tint assumed by the solution. The number of measures of acid employed is then observed, and the amount of nitrate of potassa to which they correspond, calculated. 40 parts (1 eq.) of sulphuric acid (SO_3) correspond to 101 parts (1 eq.) of nitrate of potassa, as may be seen by the following equation, which exhibits the action of the carbon upon the nitrate of potassa:—



where it will be seen that every equivalent of nitrate of potassa produces an equivalent of carbonate, which requires also one equivalent of sulphuric acid for its neutralization. The chloride of sodium is merely added to the mixture to moderate the violence of the deflagration.

A fallacious result will be obtained by this method, if the specimen examined contain sulphates, as they are reduced to sulphides by fusion with charcoal; these being decomposed by sulphuric acid (with disengagement of hydrosulphuric acid), their presence will involve the use of an excess of the test acid, and a consequent excess in the calculated percentage of nitre. If hydrosulphuric acid is, therefore, detected upon the first addition of acid to the solution of the fused mass, recourse must be had to some one of the other methods.

Pelouze's method consists in boiling a known weight of the salt with a solution of chloride of iron (FeCl_2) containing excess of hydrochloric acid (prepared by dissolving piano-wire in excess of acid), diluting largely with water, and ascertaining, by the careful addition of a standard solution of permanganate of potassa, how much iron has been converted into sesquichloride by the nitrate of potassa, when the calculation will proceed according to the equation:—



which shows that, for every 6 equivalents (168 parts) of iron converted into sesquichloride, 1 equivalent (101 parts) of nitrate of potassa is present in the specimen.

The impurities which may exist in commercial nitre are, besides organic matter, lime, magnesia, soda, sulphuric and hydrochloric acids. In testing for these substances, the course prescribed for systematic qualitative analysis, in another part of this work, may be followed.

GUNPOWDER.

§ 149. Gunpowder is an intimate mixture of nitre, charcoal, and sulphur, the proportions of which vary somewhat in different countries, and according to the uses to which the powder is applied. The action of this substance as a propelling agent is dependent upon the rapid oxidation of the charcoal by the nitre, and the consequent sudden evolution of a large volume of heated gas. In a mixture of nitre and charcoal alone the oxidation (deflagration) proceeds with comparative tardiness; the addition of sulphur greatly augments the combustibility of the mixture (in consequence of the low temperature at which it ignites);

the sulphur, by its presence, also renders available for the oxidation of the carbon an extra amount of oxygen, namely, that which is united with the potassium, the latter being at once converted into sulphide, upon ignition of the powder.

The advantages possessed by gunpowder, as a propelling agent, over all other explosive mixtures, or over the chemical compounds endowed with explosive properties, with which we are at present acquainted, are, first, the comparative safety with which it may be manufactured, handled, and transported, and secondly, the *gradual* nature of its decomposition, when compared with that of other explosives, whereby the force resulting from the rapid evolution of gas in a confined space has sufficient time to overcome the inertia of the projectile, which is not the case with compounds, the conversion of which into gaseous products is instantaneous.

The gunpowder which is most powerful as a propelling agent is found to be that which corresponds most nearly in composition to the formula



The theoretical decomposition of a powder of this description would be represented by the equation:—



In practice, it is found that small quantities of many other products are invariably formed, besides carbonic acid, nitrogen, and sulphide of potassium, among which may be mentioned, carbonic oxide, hydrosulphuric acid, bisulphide of carbon vapor, carbonate of potassa, cyanide (and sulphocyanide) of potassium, and aqueous vapor.¹ The most important products of a careful and complete combustion, on a small scale, of powder of the above composition, have, however, been found to correspond pretty closely to the above theoretical expression.

The gases disengaged in the combustion of this powder would occupy, at 32° F. (0° C.), a volume 329 times as great as that occupied by the powder; the force exerted by the evolution of these gases is, however, mainly dependent upon their enormous expansion, at the instant of the explosion, by the heat evolved in the action; for it is calculated that one volume of powder of the above composition yields, at the moment of ignition, at least 2000 times its volume of gas.²

If gunpowder contain more carbon in proportion to the nitre than the quantity above stated, a proportionate amount of *carbonic oxide* is produced in its explosion; thus, if *six* equivalents of carbon be employed, instead of *three*, to one equivalent of nitre, the whole of the oxygen contained in the latter would

¹ The great heat attending the explosion converts a quantity of the sulphide of potassium into vapor, which takes fire with a flash at the muzzle of the gun, and is converted by the oxygen of the air into sulphate of potassa, which forms the white smoke observable after the discharge.

Chevreul examined the products obtained by the combustion of pulverized gunpowder in a small copper tube. Gay-Lussac obtained the gases by letting the powder fall, grain by grain, into the redhot tube; in both cases the gases were collected over mercury. The following are the results obtained by these chemists:—

GAY-LUSSAC.		CHEVREUL.	
Carbonic acid	58	Carbonic acid	45.41
Carbonic oxide	42	Nitrogen	37.53
Nitrogen	5	Nitric oxide	8.10
	100	Carbonic oxide	4.87
		Carburetted hydrogen	3.59
		Hydrosulphuric acid	0.50
			100.00

² The temperature evolved by the combustion of gunpowder has been found to be sufficiently intense to fuse gold and other metals; it is estimated at 1200° C. (2192° F.)

theoretically be evolved as carbonic oxide on the decomposition of the powder, as the following equation shows:—



Now since the space occupied by equal equivalents of carbonic oxide and of carbonic acid is the same, it is evident that a much larger volume of gas would be evolved (calculated for a temperature of 32 F. and ordinary barometric pressure) from the gunpowder which contained the larger amount of charcoal. But it must be borne in mind that the amount of heat evolved in the production of carbonic oxide is far less than that generated when carbonic acid is produced, and that, consequently, the powder which contains the minimum quantity of charcoal will yield, *at the instant of explosion*, by far the greatest bulk of gas. That this expansion of the gas by heat is of the greatest importance, is very evident from what has already been stated; it has been ascertained that this expansion increases greatly with an increase of temperature; thus, for example, 200 volumes of gases raised to a temperature of 2428° F., occupy the same bulk as 300 volumes which are only heated to 1466°·6 F., namely, 1170 volumes.

It will be readily seen, from the above considerations, why a powder which approximates most nearly in composition to the formula $\text{KO.NO}_3 + \text{C}_s + \text{S}$ should be most valuable for fire-arms. The percentage composition of gunpowder of this description would be:—

Nitre	74.82
Charcoal	18.33
Sulphur	11.85
	100.00

Upon comparing the composition of the powders prepared in different countries¹ for fire-arms, they will be found to agree more or less closely with the above percentages; it must be remembered, however, that the proportions have been arrived at by experience, in most cases long before any theory concerning the chemical composition or action of powder was advanced. In some cases the deviations from the theoretical numbers may be readily explained; thus, in the manufacture of the Waltham Abbey powder, a slight excess of charcoal is always employed, in order to allow for the small quantity of foreign matter (*ash*) always associated with carbon in that form, while the proportion of sulphur is reduced as much as is compatible with the production of a powerful powder, in consequence of the injurious action of that substance (and even of sulphides, in the presence of moisture) upon metal.

Some kinds of powder, manufactured for special purposes (*e.g. blasting-powder*), contain a much larger proportion of charcoal; the expense of the powder is there-

¹ The following table shows the percentage composition of gunpowder of different countries:—

	Nitre.	Charcoal.	Sulphur.
English (<i>Waltham Abbey</i>)	75.00	15.00	10.00
France, Prussia, United States, }	75.00	12.50	12.50
Russia	78.78	18.59	12.63
Austria	76.00	11.50	12.50
Spain	76.47	10.78	12.75
Switzerland (<i>Champy globular powder</i>)	76.00	14.00	10.00
Sweden	75.00	9.00	16.00
China	75.00	14.40	9.60

by considerably diminished, a matter of primary importance in such cases. In the decomposition of such powder, a mixture of carbonic oxide and carbonic acid gases is evolved, and a higher sulphide of potassium produced. The comparative force exerted by a powder of this description is of course far less than that exerted by good fire-arm powder.

MANUFACTURE OF GUNPOWDER.—In the manufacture of gunpowder the minute state of division and intimate mixture of the ingredients is of equal importance with the proper proportions; hence considerable care must be bestowed upon the various processes through which the constituents and the powder itself have to pass. Different methods have been employed from time to time, for attaining the desired results. We shall confine ourselves chiefly to an outline of the manufacture of gunpowder, as conducted at the Waltham Abbey mills.

The Ingredients.—The greatest care is taken in the preparation of pure ingredients for gunpowder.

The presence of any chloride in the *nitre* employed must be avoided, since the deliquescent nature of these salts would act very injuriously upon powder, causing it to absorb moisture, whereby its power is soon greatly weakened. Saltpetre containing more than $\frac{1}{3500}$ of chlorides is rejected as unfit for use. By the method adopted at Waltham Abbey, of which an outline has already been given (§ 145), the nitre is obtained absolutely pure. In order to free it perfectly from moisture, it is always very carefully fused and cast into moulds. In this operation, the application of too high a temperature is guarded against with care, since the production of a small quantity of caustic potassa, by the decomposition of the nitre, would impart deliquescent properties to the latter.¹

Carefully prepared *flowers of sulphur* are employed in the manufacture of gunpowder. The method of obtaining these at Waltham Abbey is similar to that described at § 103. When the walls of the chamber into which the sulphur-vapors are conducted become too warm to effect their proper condensation to flowers, the communication between the chamber and the retort is closed, and another one opened, leading into a metal receiver; the sulphur is allowed to distil over into this,² until the chamber has become sufficiently cool, and the flowers have been collected from its sides, when the vapors are once more allowed to pass into it.

Since, at the commencement of the distillation, when the retort and condensing-chamber still contain atmospheric air, the first portions of the sulphur-vapor must inflame, sulphurous acid being produced, the flowers will frequently possess a faint acid reaction when they are removed from the chamber. This is avoided by allowing the sulphur to condense upon damp cloths, or removed by allowing it to remain between such cloths for a short time previously to use.

The charcoal for powder is carefully prepared in retorts and slips, as described at § 121. The volatile products are conducted from the retorts, by pipes, into the fire by which the charring is effected, and there consumed. The species of wood exclusively employed by government for making powder-charcoal, are alder, dogwood,³ and willow. About twenty-five to thirty per cent. of charcoal are

¹ The following is a delicate test for the *over-fusion of nitre*: a small quantity of the fused nitre is dissolved in water, and a few drops of a neutral solution of sulphate of copper added. The production of a bright-green tint indicates the presence of nitrous acid (nitrite of copper being produced), and shows that a portion of the nitre has at any rate undergone the first stage of decomposition (*see Nitrate of Potassa*): if, in addition, a flocculent blue precipitate (hydrated oxide of copper) is formed immediately upon the addition of the sulphate of copper, or is deposited after a short time, the presence of caustic potassa in the sample is indicated.

² The massive (crystalline) sulphur thus obtained is employed by government in the manufacture of other laboratory compositions.

³ Dogwood charcoal is employed exclusively for rifle-powder.

generally obtained in successful operations.¹ Good powder-charcoal should have a bluish-black appearance, and, when powdered, a lustre resembling that of velvet; it should be light, sonorous, firm, and slightly flexible. The wood used in the manufacture of powder-charcoal, as also the charcoal itself, must be carefully picked over, as directed at § 121 (*Cylinder-charcoal*).²

Pulverization and intimate mixture of the Ingredients.—The machine or mill by which the ingredients are first powdered, and afterwards intimately blended, or *incorporated*, as it is termed, consists of two upright mill-stones, or runners, of smoothly cut marble or limestone, or of iron (about 7 feet in diameter, and 12 inches thick, and weighing from 3 to 4 tons each), which turn upon one common horizontal axis, while this again turns upon a vertical axis, placed in the centre of a flat bed, of the same material as the runners that revolve upon it.³ The

¹ The charge for a retort, at Waltham Abbey, is 1½ cwt., which is burnt from three and a half to four hours; the charcoal obtained generally amounts to 40 lbs.

² The superiority of a product of less complete carbonization of wood, called *charbon roux* (red charcoal), over the black charcoal, for the manufacture of gunpowder, has been maintained by some chemists, particularly in France. The subject still requires experimental investigation; we may however state, in a few words, what is known concerning it. A full red heat yields black charcoal containing about 90 per cent. of carbon, and 7 to 8 per cent. of hydrogen compounds. A temperature approaching red heat yields *charbon roux*, containing 70 to 72 per cent. of carbon, and 28 to 30 per cent. of hydrogen and oxygen. The latter appears to be charcoal containing the maximum amount of *inflammable matter* in wood.

Powder made with this kind of charcoal certainly appears to burn with greater energy than that made with black charcoal; this arises, probably, from the readier inflammability of the charcoal.

In *charbon roux*, there appear to exist about 28 per cent. of hydrogen and oxygen in the proportion to form water, besides about 2 per cent. of hydrogen over and above that amount. A larger proportion of charcoal must therefore be employed to effect the proper decomposition than if black charcoal were used, since the large percentage of hydrogen and oxygen above alluded to does not enter into the action; for in the combustion of organic substances, the heat is produced by the combustion of the carbon and of that amount of hydrogen present in the body, over and above the quantity required to produce water by the oxygen present in the substance. The produce thus obtained would be far less dense than ordinary powder, it would therefore occupy a greater bulk, and would be liable to dust very much, and also attract considerably more moisture than black charcoal powder. Moreover, the specific heat of aqueous vapor is very high, and a large amount of the heat generated in the explosion of the powder would consequently be absorbed in the conversion of the water into vapor; hence it is impossible that the expansion of the gases should be equal to that of the products obtained in the combustion of black charcoal gunpowder.

³ Other forms of machinery are employed in different parts of the Continent for pulverizing and mixing the ingredients. One of these consists of a drum or cylinder of wood or leather, strained over a frame, revolving on central axes. Projecting ridges of wood are fixed on the internal surface of the drum, at a short distance from each other. The coarsely-crushed ingredients are introduced into the drum through a flap-door, together with a number of small balls (of bronze, or a harder alloy, ¾ copper to 1 tin). The barrel is then allowed to revolve with moderate rapidity, whereupon the balls are raised to a certain height, and then fall back from ridge to ridge, crushing the material with which they meet. This is termed the *revolutionary process*, having been adopted in France at the time of the first Revolution. In some parts of the Continent, the manufacture of powder is effected by *stamping-mills*, which consist of long rows of circular mortars of iron or of oak (with very hard wood inserted in the bottoms); long pestles, fitted with bronze shoes (weighing about 60 pounds), and provided, at the centre of the rod, with crosspieces, are lifted to a certain height (about 1½ foot) by the projections of a long cog-wheel, and then allowed to fall upon the ingredients in the mortar. The pestle is lifted about sixty times in a minute: the mass to be pulverized or incorporated is moistened with water from time to time. The mortars being so formed as to contract gradually from the centre towards the opening, the mass, as it is forced up the sides of the mortar by the blows of the pestle, falls back again to the bottom; in this manner the mass becomes thoroughly mixed: to insure this result, it is, however, necessary to loosen, from time to time, the hard crust that will always form at the bottom of the mortar.

cylinders are not equidistant from the vertical axis; they do not consequently move over the same surface.¹

The ingredients, having been reduced to a sufficiently fine state of division, are weighed out, for mixture, in the following invariable proportions:—

Nitre	81 lbs. 8 oz.
Charcoal	6 " 4 " 13 drms.
Sulphur	4 " 3 " 3 "
<hr/>	
Together	42 " 0 " 0 "

which constitute what is termed a *charge*, or the quantity of material placed at one time upon the incorporating-mill. These quantities are then introduced into the *mixing-machine*, which consists of a wooden box, or cylinder, through which passes an octagonal shaft, provided with a number of fan-like arms. The cylinder is made to revolve round the shaft, which turns at the same time in the opposite direction. From five to ten minutes are allowed for effecting a thorough mixture of the ingredients; the powder is then removed from the cylinder and filled into bags, which are tied firmly, so as to prevent any separation of the ingredients from each other in their transport to the incorporating-mills.²

The mixture is then spread upon the bed of the incorporating-mill, moistened with distilled water to such an extent as to make the particles cohere firmly,³ and once more submitted to the action of the mill. The runners are not allowed to revolve so rapidly as in the first instance, when the ingredients are merely ground, in order that the particles may be uniformly submitted to the crushing action and pressure of the rollers for a longer period. Great care must be taken that no hard or gritty particles fall upon the bed of the mill, and the mass must be retained in a sufficiently moist state throughout the incorporation, which lasts from three to four hours. A can with a very fine rose is employed for moistening the powder; any particles that are pushed by the rollers beyond their track, are carried back by scrapers, which are appropriately fixed, and travel round with the rollers. Towards the close of the operation, the latter are allowed to revolve only very slowly.

The mass that is removed from these mills after incorporation, is now possessed of all the chemical properties of powder, the particles having become most uniformly and intimately mixed. It soon hardens, forming cakes of about $\frac{1}{2}$ inch thick, which should have a dark grayish-black appearance, and be perfectly homogeneous, exhibiting no specks whatever. In this state the powder is called *mill-cake*.

These cakes, before they are thoroughly dry, are reduced to coarse powder, in what is called the *breaking-down* mill (which consists of two sets of metal rollers, furnished with teeth, between which the powder passes); this is then placed in layers of a certain thickness between copper plates, and packed in very stout boxes, in which it is submitted to a pressure of 122 tons on the square foot, by means of a powerful hydraulic press. When the powder is removed from between the plates, it presents very much the appearance of slate, being in very

¹ Any portions of the ground substance adhering to the rollers is removed, as they revolve, by scrapers of wood, tipped with iron, which are fixed within sufficiently close proximity to the surface of the roller.

² If a mixture of this description, or a gunpowder that has not been subjected to sufficient pressure, be but loosely packed, the comparative densities of the ingredients being very different, they will gradually separate to a great extent, if subject to any concussion in their transport; the light charcoal-powder will collect on the upper surface, and much will escape, as dust, through the fissures in a box, or between the interstices of a sack.

³ The quantity of water required for this purpose varies considerably with the temperature and state of the atmosphere.

dense blackish cakes, about $\frac{1}{4}$ inch thick (called *press-cake*). By subjecting the powder to this powerful pressure, several important results are attained. The density of the powder is very greatly increased, and consequently a certain bulk of the pressed powder will yield, upon combustion, a far greater volume of gas than an equal bulk of powder that has only been subjected to the pressure of the incorporating-mill. Moreover, the hardness of the powder is naturally increased in a similar proportion, whereby it is better enabled to withstand the action of the atmosphere, and is also far less liable to loss from dusting, in its transport.

Granulation of the Powder.—By this process the powder is obtained in grains of the various sizes and forms required for fire-arms of different descriptions, or for other purposes (*e. g.* in blasting operations), the fineness of the powder determining to a great extent the rapidity of combustion, which requires modification according to circumstances.

A very ingenious piece of machinery is employed at Waltham Abbey for granulating the powder, and separating it into the different kinds, known as *large grain* (or L. G.), *fine grain* (or F. G.), and *meal-powder*, or dust. It does not come within our province to give more than a sketch of the principle of this machine.

A continuous supply of the coarsely-crushed press-cake is allowed to fall upon a pair of revolving metal rollers, provided with large teeth, whereby it is partly reduced to grains of different sizes; the powder, as it passes from these rollers, is received by a set of three long, sloping screens, or sieves, of different fineness, fitted one upon the other, and working continually backwards and forwards, with a trough, running their whole length at the bottom. The powder is thus subjected to the usual sifting motion; those portions that are retained by the first sieve, as they work their way down its surface, are made to fall between a second pair of rollers with finer teeth, the powder granulated by these again falls upon the upper screen, where it is once more sifted; any portions that may still be too coarse to pass through, are reduced by a third, still lower, set of rollers with very fine teeth. The powder, on passing through the first screen falls upon the second, where the large-grain powder is retained, being separated from the fine grains and dust by the sifting motion to which it is subjected; the third sieve retains the fine-grain powder, while the dust or meal-powder falls through into the trough beneath. Each kind of powder, as it travels down to the bottom of the screens, is collected at the opening in boxes, running on wheels and rails.

Various additional contrivances are applied to this piece of machinery, to obviate the necessity of the presence of workmen, during the granulation of the powder, in case of an accidental explosion.¹

After granulation, the powder is freed from dust by allowing it to run gradually through sloping reels, inclosed in boxes and covered with canvas, or with silk of about fifty-six meshes to the inch, according to the size of the grains introduced. The finest-grained powder is afterwards rounded and polished by what is termed the *glazing process*. This consists in subjecting the powder, in a sufficiently moist state, to a rotary motion in barrels or drums, containing arms

¹ On the Continent, the powder is chiefly granulated in drum-sieves of different fineness, fitting one in the other, to which an alternating rotary motion is imparted. On the upper of these is placed, together with the crushed powder, a lenticular disk of heavy wood (sometimes loaded with lead). By the motion of the drum, this disk is made to travel over the surface of the upper sieve, crushing the particles of the powder with which it meets until they are all sufficiently fine to pass through the first sieve.

The so-called *Champy*, or Swiss *globular powder*, is obtained by allowing minute drops of distilled water to fall from a very finely perforated tube upon meal-powder, which is made to revolve in a drum, such as has been already described as used sometimes for powdering and mixing the ingredients. Each drop of water thus collects, in a globular form, a certain quantity of the powder; the grains thus formed are afterwards separated from the dust by means of sieves.

similar to the mixing-drums already described, the velocity of the motion being only sufficient to allow the grains to roll over each other and become polished by attrition. Powder thus glazed is less liable to dust in its transport, and is rendered more impervious to the action of atmospheric moisture. Very coarse-grained powder (blasting-powder) is sometimes glazed with graphite.

The last operation which the powder has to undergo, is that of *desiccation*. It is requisite during all the processes enumerated to retain the powder in a more or less moist state; it is, however, necessary when the manufacture is completed to expel the moisture. For this purpose the powder is exposed for some time to a temperature of 134° F. in a chamber heated by steam, and so constructed that there shall be a continual change of atmosphere, the moist air escaping as dry air enters.

The greatest precautions are adopted to prevent accidents during the manufacture of powder, or at any rate to prevent a fire in one part of the factory extending to any other portion. Each process is conducted, if possible, in detached premises at some distance one from the other, and in some cases these are flanked by high buttresses of brick or stone, of great thickness. All kinds of grit are most carefully excluded from the various buildings, the floors of which are frequently covered with leather, and into which no person is permitted to enter in shoes that have been worn out of doors. Nevertheless, terrible accidents occur at times, the affinities between the constituents of powder being balanced with such nicety that trifling causes, such as comparatively slight friction, are sometimes sufficient to impart to it the impulse necessary for its decomposition.

Properties of Gunpowder.—Good powder should exhibit perfect uniformity of texture; light specks or glittering points indicate an incomplete mixture. The grains should be sufficiently hard not to be easily crushed between the fingers, and not to soil these or a piece of paper by mere contact. Gunpowder should burn rapidly, leaving a very slight residue. If inflamed upon white paper, it should blacken the latter but slightly, and should on no account set light to it. Powder is inflamed by any burning substance, by an electric spark, or red-hot metal, or by violent concussion. It does not, however, ignite if exposed to a temperature below a red heat. If it be exposed in a glass vessel, containing an atmosphere of hydrogen or carbonic acid, to a gradually increasing temperature, the sulphur may be completely separated, subliming upon the cool portion of the vessel.

It has been proved that powder may be inflamed not only by the powerful concussion of iron against a hard substance, but by the concussion of comparatively soft bodies, provided it be sufficiently powerful. Experiment has shown that powder placed upon lead, or even wood, may be ignited by the concussion of a leaden bullet fired at it.

The inflammability of powder is greatly influenced by its physical nature, as has been already stated. A fine-grain powder will burn more rapidly than large-grain powder; the greater the density of a powder, the more gradual its combustion.

Angular powder will burn more rapidly than round-grained powder; glazing also decreases the inflammability of powder. The presence of moisture naturally retards the inflammability of powder considerably.

Powder in which the theoretical proportions are exact, and in the manufacture of which a very inflammable charcoal has been used, the ingredients having been mixed without the application of very great pressure, will undergo, when ignited, an almost instantaneous decomposition: such a powder resembles the fulminates in many respects, the strain which it exerts upon the fire-arm is far too powerful, hence it is not so generally applicable as powder which undergoes a more gradual decomposition.

(Gunpowder always attracts moisture, more or less, since charcoal, however

dense, absorbs moisture from the air, though of course the hygroscopic property of powder is considerably increased by the use of porous charcoal (such as *charbon-roux*) in its manufacture, or by the presence of any considerable quantity of powder-dust. Powder, manufactured with perfectly pure nitre, is found, if preserved in dry stores, to absorb about 0.5 per cent. of moisture; the amount naturally increases considerably if the powder is kept in a damp situation. Fine grain powder is generally found to absorb moisture more rapidly than the large-grain powder.

The amount of ash left upon the ignition of powder varies considerably with the purity of the ingredients, with the proportions employed, and particularly with the nature of the charcoal used. Its gradual accumulation in a fire-arm is a source of great inconvenience, since it soon renders it foul and difficult to charge, thus limiting the number of rounds that can be fired in rapid succession, *i. e.* without first cleaning out the fire-arm. This *fouling*, as it is termed, is avoided to some extent by the use of a small quantity of some fatty substance, which lubricates the barrel, and, by preventing the adhesion of the ash, promotes its expulsion by the gases as they make their escape.

For the analysis of gunpowder, *see* Quantitative Analysis, special methods.

§ 150. NITRITE OF POTASSA (KO.NO_2) is sometimes employed for the preparation of nitrogen; it may be obtained sufficiently pure for this purpose by maintaining nitrate of potassa at a red heat in an earthen crucible, until, a small portion being removed and dissolved in water, the solution has an alkaline reaction, and gives a brownish-white precipitate (a mixture of nitrite of silver and oxide of silver), with nitrate of silver, showing that a little potassa has been set free. The pure salt may be prepared by decomposing, with chloride of potassium, the nitrite of silver previously purified by recrystallization.

It is a deliquescent salt, which crystallizes with considerable difficulty.

CHLORATE OF POTASSA, HYPEROXYMURIATE OF POTASSA, KO.ClO_3 ,

§ 151. *Preparation.*—The simplest method of preparing this salt consists in transmitting, through a wide tube, a current of washed chlorine into a concentrated solution of potassa or its carbonate; the solution, when saturated with chlorine, is heated for some time, to insure the complete conversion of any hypochlorate into chlorate, and allowed to cool, when chlorate of potassa crystallizes out, and may be purified by recrystallization. The action of the chlorine upon the potassa, in this process, is thus represented:—



A more economical method consists in passing chlorine over a somewhat damp mixture of 7.6 parts of carbonate or sulphate of potassa and 16.8 of hydrate of lime; the mass is afterwards treated with boiling water, and the chlorate of potassa separated from the chloride of calcium by crystallization.¹

Properties.—Chlorate of potassa crystallizes in colorless, thin, tabular crystals, and, more rarely, in needles, which contain no water of crystallization, and are

¹ Calvert has proposed an improved process for the manufacture of chlorate of potassa, which consists in employing a solution of caustic potassa of spec. grav. 1.11.—3.1 parts of this solution are mixed with 1 part of hydrate of lime, previously slaked; the mixture is slightly heated, and rapidly saturated with chlorine. The solution is filtered, to separate any slight insoluble residue, and evaporated to crystallization.

The great advantage consists in the circumstance that the chlorine is oxidized at the expense of the lime, the calcium of which is converted into chloride, so that nearly the whole of the potassa is converted into chlorate:—



unaltered by exposure to air. When heated, they decrepitate, fuse easily, and at a temperature below redness evolve oxygen (the details respecting this decomposition will be found under the Preparation of Oxygen, § 69).

It has also been observed, in the place referred to, that if the salt be mixed with certain substances, especially with binoxide of manganese, the decomposition is promoted in a very remarkable manner. The oxygen evolved from chlorate of potassa has generally an odor of chlorine.

Chlorate of potassa is soluble in about 17 parts of water at the ordinary temperature (with production of cold); at the boiling point, it dissolves in 1.5 parts of water, so that the greater part is deposited on cooling; it is sparingly soluble in alcohol.

The chlorate, like the nitrate of potassa, possesses oxidizing properties, but much more powerful than those of the latter salt; if sprinkled upon red-hot coals, it gives rise to vivid deflagration. If a mixture of chlorate of potassa with sulphur be triturated, or struck with a hammer, explosion ensues; various metals, metallic sulphides, and organic substances also form explosive mixtures with chlorate of potassa; a mixture of chlorate of potassa and sugar is inflamed when moistened with oil of vitriol, and this principle was formerly taken advantage of in the preparation of the Promethean matches.

When acted upon with conc. sulphuric acid, an experiment which requires great caution, chlorate of potassa is decomposed with violence, yielding perchlorate of potassa, peroxide of chlorine, and sulphate of potassa; thus:—



Nitric acid converts it into a mixture of nitrate and perchlorate of potassa, with evolution of chlorine and oxygen:—



When heated with hydrochloric acid, a decomposition takes place which is not perfectly understood, and which results in the production of a deep yellow pungent gas, which was named by Davy *euchlorine* (see § 94).

A mixture of chlorate of potassa with hydrochloric acid or nitric acid is frequently employed as an oxidizing solvent in analytical operations.

Uses.—Chlorate of potassa is extensively employed for the manufacture of lucifer matches. For this purpose it is generally mixed with nitrate of potassa, phosphorus, minium, and gum.¹

The intense power exhibited by chlorate of potassa as an oxidizing agent, in which respect it far surpasses the nitrate of potassa, has induced many experimenters, from a comparatively early period, to attempt the production of a compound containing chlorate of potassa instead of nitre, which would possess all the properties of gunpowder, while it was far more powerful, effecting results which could only be obtained by the use of a much larger comparative amount of powder. All experiments hitherto made have shown, however, that explosive mixtures of chlorate of potassa with easily oxidizable substances (*e. g.* sulphur, sulphide of antimony, &c.), resemble, in the effect they produce, the fulminates much more than they do gunpowder, their decomposition being too instantaneous to admit of their use in fire-arms (see § 149); the strain exerted by the explosion of the least powerful of such mixtures upon the barrel of a gun has been found too great to be withstood by the metal for any lengthened period. Several mixtures have been proposed (*e. g.* the so-called *white gunpowder*, consisting of chlorate of potassa, sulphur, and ferrocyanide of potassium), particularly for blasting purposes, where they might meet with more successful application, were it not for the very great risk attending their manufacture on a large scale, in conse-

¹ In matches which ignite without explosion, the chlorate of potassa is replaced by a mixture of nitrate of potassa and binoxide of lead.

quence of the slight impulse required to induce the violent action of chlorate of potassa.

As detonating compounds, however, where an instantaneous action is required (e. g. in firing a charge of powder), these mixtures are very useful, and receive extensive application, being far cheaper than the fulminates.

Thus, the composition with which the percussion-tubes for cannon are filled, consists of 2 parts of chlorate of potassa, 2 parts of sulphide of antimony, and 1 of powdered glass (to increase its susceptibility). Mixtures of this description must be made with great care. The ingredients are first powdered separately, and then mixed with a feather, or some comparatively soft body, in a smooth vessel. Chlorate of potassa is also occasionally used in medicine.

§ 152. PERCHLORATE OF POTASSA, $KO.ClO_3$. This salt exists in the residue left on gently heating chlorate of potassa till the evolution of oxygen slackens; if this residue be boiled with water, the solution, on cooling, deposits crystals of the perchlorate.

Perchlorate of potassa forms anhydrous, colorless, prismatic crystals, which are decomposed by heat into chloride of potassium and oxygen. They are sparingly soluble in cold, but more so in hot water; perchloric acid is hence occasionally employed as a test for potassa. Perchlorate of potassa is more stable than the chlorate; it deflagrates with redhot charcoal, but not so powerfully as the latter salt. It merely evolves perchloric acid when heated with sulphuric acid, and does not turn yellow when treated with concentrated hydrochloric acid.

§ 153. HYPOCHLORITE OF POTASSA ($KO.ClO$), in the pure state, is known only in solution, prepared by mixing aqueous solutions of hypochlorous acid and potassa at a low temperature.

The solution known as *Eau de Javelle*, contains equivalent proportions of chloride of potassium and hypochlorite of potassa, and is prepared by passing chlorine into a very cold, dilute solution of potassa, or its carbonate, so as to leave the alkali slightly in excess; or, more conveniently, by decomposing the solution of the corresponding lime-compound with carbonate of potassa. The solution evolves chlorine when treated with acids, and possesses powerful bleaching properties; it is sometimes used as a bleaching agent and disinfectant.

If a deficiency of chlorine be passed over moist carbonate of potassa, a mixture of the above compound with bicarbonate of potassa is obtained.

§ 154. BROMATE OF POTASSA ($KO.BrO_3$) is prepared by a process similar to that for the chlorate, which it resembles in most of its properties.

IODATE OF POTASSA ($KO.IO_3$) is prepared by a somewhat similar process; when heated, this salt evolves oxygen, and vapors of iodine, leaving a residue containing potassa, and iodide of potassium.

There are two acid iodates of potassa, the formula of which are, respectively, KO_2IO_3 , and KO_3IO_3 .

The former of these combines with chloride of potassium, and bisulphate of potassa.

PERIODATE OF POTASSA ($KO.IO_4$) resembles the perchlorate in properties, and may be prepared by passing chlorine through a solution of iodate of potassa, mixed with caustic potassa.

SULPHATE OF POTASSA, $KO.SO_4$.

§ 155. This salt is prepared from the residue (of bisulphate) left after the preparation of nitric acid; this residue is dissolved in hot water, and the solution neutralized with carbonate of potassa; the sulphate crystallizes out on cooling. It forms hard, colorless prisms, free from water. When heated, these crystals decrepitate, and fuse at a red heat, but are not decomposed. Sulphate of potassa is sparingly soluble in water, and insoluble in alcohol. Its solubility increases steadily as the temperature rises.

BISULPHATE OF POTASSA ($\text{KO.SO}_3, \text{HO.SO}_3$) constitutes the residue obtained in the preparation of nitric acid from equal weights of nitrate of potassa and oil of vitriol. This salt crystallizes in rhombic prisms, which deliquesce in air, and are very soluble in water, yielding a solution which has a very acid taste and reaction.

This salt is sometimes employed as a flux in mineral analysis, and is also useful for cleaning vessels of platinum. It fuses at a low temperature, and if strongly heated, is converted into the neutral sulphate. The equivalent of hydrated acid present in this salt, acts very much as if it existed in the free state.

Other compounds of sulphate of potassa and sulphate of water are said to exist.¹

The *phosphates of potassa* are not possessed of any practical interest.

CARBONATE OF POTASSA, SALT OF TARTAR, POTASHES, PEARLASHES.



§ 156. Carbonate of potassa exists in the residue left on incinerating various inland plants; these contain potassa in combination with various organic acids, forming salts, the acid of which is decomposed at a high temperature, leaving the potassa in the form of carbonate.

Preparation.—From the ashes of land-plants, the carbonate of potassa is extracted by lixiviation with water (*see* Nitre); the lye is evaporated to dryness, and the residue calcined in a reverberatory-furnace till the organic matter has burnt off, when a mass is left, which is known as *crude potashes*; it contains about 60 per cent. of alkaline carbonate, mixed with various mechanical and insoluble impurities, together with much chloride of potassium, sulphate and silicate of potassa, and has also, generally, a greenish-blue color, due to manganate of potassa. In order to purify this substance, it is exhausted with a little water, filtered, evaporated, the sulphate of potassa allowed to crystallize out, and the liquid evaporated to the crystallizing point of the carbonate; the product thus obtained is that known as *pearlash*.²

Salt of tartar is a purer kind of carbonate of potassa, obtained by calcining the bitartrate.

The purest carbonate of potassa, for chemical purposes, is obtained by igniting the binoxalate of potassa, which is prepared by adding an excess of oxalic acid to hydrate of potassa, and purifying by recrystallization.

Properties.—Carbonate of potassa may be crystallized, on cooling, from a very concentrated hot solution, in indistinct rhombic octohedra, of the formula $\text{KO.CO}_2 + 2\text{Aq}$. When heated, these lose their water, and the dry carbonate fuses, unchanged, at a bright red heat. This salt deliquesces when exposed to air, and dissolves in less than its own weight of water; the solution is powerfully alkaline and corrosive. It is insoluble in alcohol.

Uses.—Carbonate of potassa is very largely used in the manufacture of soap and glass; it is also employed as a detergent, and as the source of most of the salts of potassa. In the rectification of spirit of wine, fused carbonate of potassa is sometimes used to abstract the water. The chemist employs it in mineral analysis, and it is frequently administered medicinally.

Since carbonate of potassa is so important an article of commerce, it is neces-

¹ It has been lately found that sulphate of potassa is capable of forming definite compounds with some other hydrated acids, especially with nitric and phosphoric acids.

² The carbonates of potassa and soda may be readily freed from silica by evaporating their solutions to dryness, with addition of carbonate of ammonia; on redissolving the residue in water, the silica is left. This fact is of importance for the preparation of the pure hydrated alkalies.

nary to be able to ascertain the real value of any particular specimen, which, of course, depends upon the amount of pure carbonate of potassa which it contains. The process by which this is effected is termed *alkalimetry* (see Special Methods of Analysis.)

BICARBONATE OF POTASSA ($\text{KO.CO}_2, \text{HO.CO}_2$) is prepared by passing carbonic acid through a cold saturated solution of carbonate of potassa, when the less soluble bicarbonate is deposited; or by passing carbonic acid over the moistened carbonate.

Properties.—Bicarbonate of potassa crystallizes from a warm solution in colorless, rhomboidal prisms, of the formula $\text{KO.CO}_2, \text{HO.CO}_2$; when heated, they lose water and carbonic acid, leaving carbonate of potassa. The bicarbonate requires 4 parts of cold water for solution, and nearly its own weight of hot water; it is insoluble in alcohol. Its aqueous solution is not nearly so alkaline as that of carbonate of potassa, into which it is gradually converted when boiled.

Bicarbonate of potassa is occasionally used in medicine, and sometimes as a source of pure carbonate of potassa.

SILICATES OF POTASSA.

§ 157. Potassa forms several combinations with silicic acid, which may be obtained by fusing the alkali or its carbonate with different proportions of silica. When these compounds contain a large excess of silica, they are insoluble in water; but if the alkali be in large proportion, the combination is soluble. The former is the case with those silicates which form the basis of the ordinary potash-glass, whilst compounds of the latter order constitute the soluble glasses which are used as varnishes to protect wood from decay and fire (see § 138).

An aqueous solution of this description, prepared from a fused mixture of 1 part of quartz-sand with 4 parts of carbonate of potassa, is sometimes also employed as a reagent.

Silicate of potassa exhibits a remarkable tendency to form double silicates.

PEROXIDE OF POTASSIUM, KO_2 .

§ 158. When potassium is heated in a current of dry oxygen, a yellow substance is produced, which is the peroxide. This compound is also formed when potassa is heated in oxygen, and is left, in an impure state, as the ultimate product of the action of heat upon nitrate of potassa. When treated with water, this substance is decomposed with evolution of heat; oxygen is disengaged with effervescence, and hydrate of potassa is found in solution. When peroxide of potassium is heated with organic matter, detonation ensues. It is deoxidized by sulphurous and phosphorous acids, and by ammonia.

CHLORIDE OF POTASSIUM, KCl .

§ 159. This salt occurs in sea-water, and in the water of many mineral springs; it is formed when potassium is introduced into chlorine, the metal taking fire; it is also produced when chlorine, or hydrochloric acid, acts upon potassa or its carbonate, the chlorine giving rise, at the same time, either to hypochlorite or chlorate of potassa, and the hydrochloric acid only to water. Potassium also decomposes hydrochloric acid, combining with the chlorine, and liberating hydrogen. Chloride of potassium is obtained as a by-product in various processes, particularly in the manufacture of soap and glass, and in the refining of nitre.

Properties.—Chloride of potassium crystallizes in white cubes, which are anhydrous and unalterable in air; when heated, they decrepitate. This salt fuses at a red heat, and is volatilized at a higher temperature. It dissolves in about

8 parts of water, producing considerable cold;¹ it is more soluble in hot water, the solubility increasing uniformly with the temperature, and almost insoluble in alcohol. Chloride of potassium is capable of combining with anhydrous sulphuric acid, forming a compound of the formula $KCl \cdot 2SO_2$. It also unites with tetrachloride of iodine. Chloride of potassium is sometimes used to convert into nitrate of potassa the nitrate of lime obtained in artificial nitrification (§ 145); it is also occasionally employed as the source of potassa in alum.

BROMIDE OF POTASSIUM, KBr.

This salt is formed under the same conditions as the chloride; it is usually prepared by dissolving a slight excess of bromine in potassa, separating the bromate of potassa by crystallization, evaporating the mother-liquid, and decomposing any bromate of potassa by igniting the residue, which may then be dissolved in water, and crystallized. The bromide crystallizes in white cubes, which are anhydrous, and behave like the chloride when heated. It is readily soluble in water, producing cold, and nearly insoluble in alcohol. A solution of bromide of potassium is capable of dissolving considerable quantities of bromine. -

Bromide of potassium is used in photography.

IODIDE OF POTASSIUM, HYDRIODATE OF POTASSA, KI.

Preparation.—The iodide of potassium is produced under similar conditions to those which yield the bromide, and may be prepared by the same process, substituting iodine for bromine. The usual method of preparing iodide of potassium, however, consists in digesting 2 parts of iodine and 1 part of iron filings in 10 parts of water, till they have combined to form a solution of a pale green color; the solution of iodide of iron thus obtained is decomposed with exactly the requisite quantity of solution of carbonate of potassa:—



The solution is filtered from the precipitated carbonate of iron, and evaporated to the crystallizing point.

Properties.—Iodide of potassium crystallizes in anhydrous cubes, sometimes opaque, but more generally transparent, which decrepitate when heated, fuse easily, and volatilize at a moderate heat. After fusion, it has an alkaline reaction. The pure salt deliquesces slightly, and dissolves very readily in less than its own weight of water, with production of cold; the solution has a very slight alkaline reaction; but if, as is often the case, the salt be adulterated with carbonate of potassa, its solution will be strongly alkaline, and the solid iodide will deliquesce rapidly in air. Iodide of potassium is dissolved by alcohol. The aqueous solution of the salt is capable of dissolving a large quantity of iodine, which gives it a deep brown color. This property is turned to advantage in the compound solution of iodine, which is used in medicine. Iodide of potassium is an important medicinal agent, especially in scrofulous diseases. It is also used in photography.

The iodide of potassium of commerce often contains, in addition to carbonate of potassa, caustic potassa, iodate of potassa, bromide and chloride of potassium.²

In order to ascertain the degree of purity of any specimen of iodide of potassium, we may employ a solution of chloride of mercury; 1 equivalent of this salt

¹ This depression of temperature, being much greater than that caused by chloride of sodium, has been applied by Gay-Lussac to the determination of the amount of the former in mixtures of the two salts.

² The iodate of potassa may be detected by adding solution of sulphurous acid, which will liberate a quantity of iodine, imparting a brown color to the solution. The other impurities in iodide of potassium may be detected by the ordinary methods of analysis.

completely precipitates 1 equivalent of iodide of potassium, in the form of the bright red iodide of mercury; thus:—



another equivalent of iodide of potassium redissolves this precipitate, so that if 1 equivalent of chloride of mercury be added to 2 equivalents of iodide of potassium, no precipitate is produced. In order to apply this principle, 1 equivalent (135.5 parts) of chloride of mercury (HgCl, corrosive sublimate), and 2 equivalents (166.1 parts) of the iodide of potassium to be tested, are dissolved in two equal quantities of water. The solution of chloride of mercury is poured from a *burette* into that of iodide of potassium, constantly stirring, till a permanent precipitate begins to appear; when this is the case, of course a little more than 1 equivalent of chloride of mercury must have been added for every 2 equivalents of iodide of potassium present, so that if the salt tested were absolutely pure, the whole of the mercury-solution should have been added, whereas an impure specimen will require only one-half, two-thirds, &c., of the solution, according to the amount of impurity present.¹

FLUORIDE OF POTASSIUM, KF.

This salt is formed when hydrofluoric acid is decomposed by potassium, hydrogen being evolved; it is best prepared by supersaturating potassa, or carbonate of potassa, with hydrofluoric acid, and evaporating in a platinum dish. It crystallizes in anhydrous cubes, which deliquesce in air, and dissolve readily in water. The solution has an alkaline reaction, and acts upon glass.

Hydrated crystals of fluoride of potassium may be produced at low temperatures.²

POTASSIUM AND SULPHUR.

§ 160. Potassium combines with sulphur, when gently heated with it, with vivid combustion, producing several sulphides of potassium.

SULPHIDE OF POTASSIUM, KS.

This sulphide is formed when hydrogen is passed over sulphate of potassa at a red heat, and also when sulphur is fused with excess of hydrate of potassa; thus:—



Preparation.—It may be prepared by heating to bright redness, in an earthen crucible, an intimate mixture of three parts of sulphate of potassa and 1 part of charcoal:—



The sulphide is thus obtained as a light red mass, containing always an admixture of a higher sulphide.

¹ A new method recently proposed by Penny (*Chem. Gaz.* October, 1852), consists in ascertaining the amount of a solution containing a known weight of the iodide, which is required to decompose a given quantity of bichromate of potassa dissolved in water acidulated with hydrochloric acid. The point at which the chromic acid is completely reduced is indicated by dipping a glass rod into the solution, and touching a drop of a solution of protosulphate of iron and sulphocyanide of potassium placed upon a white plate: when a red color is no longer produced, the decomposition is complete. 10 gra. of KO.2CrO_3 correspond to 33.3 gra. of KI.

² A *hydrofluat*e of fluoride of potassium, KF.HF, has been obtained.

If lampblack be substituted for charcoal in this process, the resulting sulphide of potassium is *pyrophoric*.¹

It may be obtained in a pure state by saturating a solution of potassa with hydrosulphuric acid, and afterwards adding a volume of the same solution of potassa, equal to that originally employed; the first operation gives rise to hydrosulphate of sulphide of potassium, $KS.HS$, which is converted, by addition of potassa, into sulphide of potassium. The solution may be evaporated to dryness in a retort, when the sulphide of potassium remains as a white crystalline mass.

Properties.—Sulphide of potassium, when heated in air, absorbs oxygen, and becomes covered with a coating of sulphate of potassa. It is volatile at a high temperature. This sulphide deliquesces in air, and dissolves rapidly in water with rise of temperature, giving a colorless solution, which possesses an alkaline reaction and a bitter taste; it is also soluble in alcohol. When exposed to air, solution of sulphide of potassium absorbs oxygen, and becomes gradually converted into a mixture of potassa with a higher sulphide, which imparts a yellow color to the solution.² When a pure solution of sulphide of potassium is mixed with dilute hydrochloric acid, hydrosulphuric acid is evolved, and the solution remains clear:—

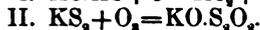
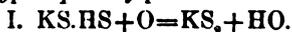


but if a higher sulphide be present, a deposition of sulphur will take place, rendering the solution milky; thus:—



Sulphide of potassium is a powerful sulphur-base (see p. 155); it combines with those metallic sulphides which play the part of acids, such as those of arsenic and antimony, to form sulphur-salts; advantage is taken of this property in analysis, where sulphide of potassium is sometimes used to dissolve the sulphur-acids, and thus to separate them from other metallic sulphides.

When a solution of potassa, or of sulphide of potassium, is saturated with hydrosulphuric acid, the compound $KS.HS$, *hydrosulphate of sulphide of potassium*, is produced, and if the solution be evaporated to a syrup in an atmosphere of sulphuretted hydrogen, and allowed to cool, the new compound may be obtained in colorless prisms, which are exceedingly deliquescent and soluble.³ The solution of this substance is strongly alkaline, and emits an odor of hydrosulphuric acid, due to the action of the atmospheric carbonic acid; if evaporated in an open vessel, it loses hydrosulphuric acid, leaving sulphide of potassium; when exposed to air, it gradually absorbs oxygen, and becomes first yellow, from the formation of a higher sulphide of potassium, and is ultimately converted into a colorless solution of *hyposulphite of potassa*.



A pure solution of hydrosulphate of sulphide of potassium, when mixed with acids, evolves hydrosulphuric acid, and remains clear.

When sulphur is heated in a solution of hydrosulphate of sulphide of potassium, hydrosulphuric acid is expelled, and a higher sulphide of potassium formed.

When an alcoholic solution of sulphide of potassium is mixed with bisulphide of carbon, an orange crystalline substance is deposited, which is known as *sulpho*

¹ It has been noticed in another place that the flash attendant upon the discharge of fire-arms is due to the combustion of the vapor of sulphide of potassium issuing from the muzzle.

² The excess of sulphur may be removed by means of finely-divided copper or silver.

³ This compound is also formed when potassium is gently heated in a current of hydrosulphuric acid, hydrogen being evolved.

carbonate of sulphide of potassium (KS.CS_2), and may be viewed as carbonate of potassa, in which all the oxygen is replaced by sulphur.

The higher sulphides of potassium, namely :—



may be prepared by fusing sulphide of potassium with the proper proportion of sulphur; they have all a yellow or brown color, and their solutions are alkaline; these yellow solutions become colorless when exposed to the air, from the formation of hyposulphite of potassa, and sulphur is deposited in all cases, except that of bisulphide of potassium; when hydrochloric acid is added to the solutions of the higher sulphides of potassium, hydrosulphuric acid is evolved, and the excess of sulphur deposited, but if a solution of one of these sulphides be very gradually added to an excess of hydrochloric acid, a portion of persulphide of hydrogen is formed at the same time, since the excess of acid gives it a certain degree of stability.

Bisulphide of potassium (KS_2) is produced when bisulphate of potassa is reduced by charcoal.

§ 161. *Hepar sulphuris*, or *liver of sulphur*, is a brown-red mass, which is sometimes used in medicine, and is prepared by fusing sulphur with carbonate of potassa in closed earthen crucibles; it varies in composition according to the proportions in which these ingredients are employed; the common proportions are two parts of carbonate of potassa to one of sulphur; the resulting mass is a mixture of *tersulphide of potassium*, hyposulphite of potassa, and sulphate of potassa, the proportions of the two latter varying according to the temperature employed.

Thus, at a low temperature, the decomposition will be represented by the equation :—



whilst, at a full red heat, a portion of the hyposulphite will be decomposed with production of *pentasulphide of potassium*, according to the equation :—



It is from *hepar sulphuris*, or some similar compound, that *milk of sulphur* is always obtained; for this purpose, the mass is prepared by fusing carbonate of potassa at rather a low temperature, with enough sulphur to produce the pentasulphide, which is, of course, mixed with hyposulphite; when an acid is added to this solution, it acts upon both these salts, precipitating sulphur, liberating hydrosulphuric acid from the pentasulphide, and evolving hyposulphurous acid from the hyposulphite; but the hyposulphurous acid is almost immediately resolved into sulphurous acid and sulphur, the latter being precipitated; the sulphurous acid, meeting with the hydrosulphuric, is decomposed according to the equation :—



so that all the sulphur is precipitated.

The most economical method of preparing milk of sulphur, therefore, consists in fusing together equal weights of carbonate of potassa and sulphur, at a temperature of about 500° F. (260° C.), when the following decomposition takes place :—



if an acid be now added to the aqueous solution of this mass :—



The *silico-fluoride of potassium*, $3\text{KF} \cdot 2\text{SiF}_6$, is sparingly soluble in water, whence hydrofluosilicic acid is sometimes employed for precipitating potassa.

The description of the compounds of potassium with cyanogen and the cyanogen-radicals, falls strictly within the province of organic chemistry.

SODIUM.

Sym. Na. Eq. 23. Sp. Gr. 0.97.

§ 162. Sodium was discovered by Sir H. Davy in soda, in the year 1807.

This metal occurs in great quantity, and very widely diffused in nature, chiefly in combination with chlorine, in the form of sea-salt, which is found not only in the waters of the ocean, but also in those of most springs. Sodium also occurs in nature in combination with oxygen and certain acids; the silicate of soda is a constituent of many minerals, such as *albite* (silicate of soda and alumina, $\text{NaO} \cdot 3\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), *analcime* (silicate of soda and alumina, $\text{NaO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 + 2\text{Aq.}$), *labradorite* (silicate of soda, alumina, and lime, $\text{NaO} \cdot \text{SiO}_2 \cdot 3(\text{CaO} \cdot \text{SiO}_2) \cdot 4(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$), *kryolite* ($3\text{NaF} \cdot \text{Al}_2\text{F}_6$), &c. The nitrate, carbonate, baborate, and sulphate of soda are found in nature. Soda is likewise found in all the animal fluids, and in plants, especially such as grow near the sea.

Sodium and its compounds are prepared from the ashes of sea-plants, and from sea or rock salt.

Preparation.—Sodium may be obtained from the hydrate of soda, by the same processes as potassium from hydrate of potassa. The process which is employed in practice, consists in converting the acetate of soda into a mixture of carbonate of soda and charcoal by ignition, and distilling this with an additional quantity of carbon, exactly in the same way as in the preparation of potassium; the preparation of sodium, however, is far easier, since it is more readily reduced, and does not form any combination with the carbonic oxide, and there is hence no fear of explosion from the choking of the tube. By a careful operator, almost the theoretical quantity of sodium may be obtained in this manner. Sodium may be purified in the same manner as potassium.

Properties.—Sodium is a yellowish-white lustrous metal, more nearly resembling silver than potassium, to which, in its other physical properties, it is very similar. Its surface tarnishes rapidly in air, from oxidation; it is therefore preserved under petroleum. Sodium fuses at 194°F. (90°C.), and distils at higher temperatures; its vapor is said to be colorless. When heated in air or oxygen, sodium burns with a bright yellow flame, and is (entirely, if the metallic surface be continually renewed by scraping) converted into soda. The specific gravity of sodium is about 0.97, so that, like potassium, it floats upon water, which it decomposes with great energy, producing soda, and liberating hydrogen; the heat is not sufficient to kindle this gas, unless the sodium be confined to one spot; for example, upon the surface of water thickened with gum, or upon moistened filter-paper; the hydrogen then burns with a fine yellow flame. Sodium being little inferior to potassium in its affinity for oxygen, may often be substituted for this metal in chemical experiments, and, since sodium is much less costly than potassium, it should always replace it if possible.

SODIUM AND OXYGEN.

Soda NaO .
Terioxide of sodium¹ Na_2O_2 .

§ 163. By the imperfect oxidation of sodium, a grayish brittle substance is produced, which is believed to be a *suboxide of sodium*, corresponding to the suboxide of potassium :—

¹ Considered by some chemists to be a sesquioxide, Na_2O_2 .

OXIDE OF SODIUM, SODA.

NaO. Eq. 31.

The pure oxide may be prepared by processes exactly similar to those employed in the case of potassium; it forms a gray mass, much resembling anhydrous potassa.

The affinity of soda for bases is less powerful than that of potassa. Its salts are, with very few exceptions, soluble in water; when neutral in constitution, they are generally neutral in reaction.

HYDRATE OF SODA. CAUSTIC SODA.

NaO.HO. Eq. 40.

Preparation.—This compound may be prepared in exactly the same way as hydrate of potassa; 3 parts of crystallized carbonate of soda are dissolved in 15 parts of water, and decomposed by milk of lime, prepared by slaking 1 part of lime with 3 parts of hot water; the decomposition is effected more easily than in the case of potassa, and the product may be purified in a similar manner.¹

Properties.—The hydrate of soda forms a white, brittle mass, which fuses easily, and volatilizes at a high temperature in white fumes; the water cannot be expelled by heat. When exposed to air, the hydrate first deliquesces, and is afterwards converted into a white mass of carbonate of soda. Hydrate of soda dissolves very readily in water and alcohol, with evolution of heat. The solution of soda thus obtained may be prepared in the same way as solution of potassa, and since it can be easily made much purer than this latter, it is frequently substituted for it. When gases, however, are passed into solution of soda, it froths up very much, so that it cannot replace hydrate of potassa in organic analysis.

The strength of this solution, like that of solution of potassa, may be inferred from its specific gravity. The spec. grav. of the most concentrated solution is about 2.00; it contains 77.8 per cent. of alkali. The description which we have given of the properties of solution of potassa, will apply to those of solution of soda. If this solution be preserved in stoppered bottles, a slip of paper should be inserted between the stopper and the neck, since the carbonate of soda, formed on exposure to the air, will otherwise cement the stopper firmly into its place.

Solution of hydrate of soda is largely employed by soap-makers for making hard soaps. This solution may be readily distinguished from solution of potassa by diluting with water, and stirring with an excess of tartaric acid, when solution of potassa gives a crystalline precipitate, whilst that of soda remains clear.

A strong solution of hydrate of soda when exposed to a low temperature, yields four-sided very fusible crystals, the amount of water in which has not been determined.

NITRATE OF SODA, CUBIC NITRE, CHILI SALTPETRE.

NaO.NO₃.

§ 164. This salt, like nitrate of potassa, occurs as an incrustation on the earth in certain hot districts (especially in Chili and Peru, where it is found in layers of considerable thickness), and may be purified from foreign matters by solution and recrystallization. It may be prepared in the laboratory by decomposing carbonate of soda with nitric acid.

¹ For soap-boiling, the lye is often made in the cold, more lime being employed; the soda is placed upon the lime, and gradually lixiviated with water.

Properties.—Nitrate of soda crystallizes in anhydrous rhombohedral crystals (whence the name cubic nitre). When heated it behaves like nitrate of potassa. Exposed to air, it deliquesces, and hence cannot be substituted for nitrate of potassa in the preparation of gunpowder. It dissolves very readily in about twice its weight of water, with depression of temperature. In its oxidizing properties, nitrate of soda resembles the corresponding potassa-salt, but does not form such powerful detonating mixtures.

Uses.—Nitrate of soda is preferred to nitrate of potassa for the preparation of nitric acid on a large scale, since it is cheaper, and yields a greater percentage of acid; moreover, the residue of sulphate of soda is a very useful salt.

Nitrate of soda is also sometimes employed for the preparation of nitrate of potassa, by double decomposition with carbonate or sulphate of potassa, or chloride of potassium. It is also occasionally used as a manure.

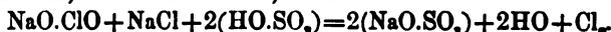
§ 165. HYPOCHLORITE OF SODA (NaO.ClO), mixed with one equivalent of chloride of sodium, and a little bicarbonate of soda, constitutes the *bleaching liquid of Labarraque*, or *chloride of soda*.

This liquid is prepared by passing chlorine through a dilute solution of soda or its carbonate, until about as much chlorine has been passed as corresponds to rather less than one equivalent for each equivalent of soda:—



The carbonic acid which is evolved at first converts the carbonate of soda into bicarbonate, a part of which remains undecomposed.

The solution thus obtained has a pale yellow color, smells faintly of chlorine, and has an alkaline reaction to test-papers, which it afterwards bleaches. When mixed with acids, it evolves chlorine; thus:—



If solution of chloride of soda be rapidly boiled, it loses its bleaching property, and is converted into a solution of chlorate of soda and chloride of sodium, for:—



Solution of chloride of soda is sometimes employed for medicinal purposes; it is also used to remove ink-stains from linen.

CHLORATE OF SODA, NaO.ClO_3 .—This salt is formed under the same conditions as the corresponding salt of potassa. Since, however, it is difficult to separate it from the chloride of sodium formed at the same time, it is best prepared by decomposing a concentrated hot solution of chlorate of potassa with solution of bitartrate of soda, when bitartrate of potassa crystallizes out on cooling, and the chlorate of soda may be obtained in cubical crystals by evaporation.

The properties of this salt are very similar to those of chlorate of potassa; it is readily soluble in cold water, and moderately so in alcohol.

§ 166. HYPOSULPHITE OF SODA, $\text{NaO.S}_2\text{O}_3$.—This salt is formed when solution of a sulphide of sodium is exposed to air, or when sulphurous acid is passed through solution of pentasulphide of sodium, until the color of the latter is destroyed.

When an aqueous solution of sulphite of soda is digested with sulphur for some days, in a closed vessel, at a moderate heat, and the filtered liquid then concentrated by slow evaporation, large prismatic crystals of hyposulphite of soda are obtained. These crystals have the formula $\text{NaO.S}_2\text{O}_3 + 5\text{Aq}$; they are unaltered by exposure to air. When heated gently, this salt fuses, water is evolved, and, at a higher temperature, sulphur escapes, whilst a mixture of sulphide of sodium and sulphate of soda remains:—



Hyposulphite of soda is readily soluble in water, but not in alcohol; its aqueous solution is neutral to test-papers, and gradually decomposes into sulphur, which

deposits, and sulphite of soda, which, with access of air, passes into sulphate of soda.

The use of this salt in photographic experiments has already been mentioned (§ 104).

SULPHITE OF SODA (NaO.SO_2) is prepared by passing sulphurous acid to saturation into a solution of carbonate of soda;¹ half the carbonic acid which is at first disengaged converts the carbonate of soda into bicarbonate, which is afterwards decomposed by the sulphurous acid with rapid effervescence; the mixture of sulphurous acid and carbonic acid, evolved by heating oil of vitriol with charcoal, may be advantageously employed for this purpose. By evaporating the solution, the sulphite of soda may be obtained in crystals, which have the formula $\text{NaO.SO}_2 + 8\text{Aq}$.

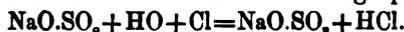
Properties.—Sulphite of soda crystallizes in transparent four or six-sided prisms, which, when exposed to air, become covered with a white crust of sulphate of soda.

When heated, this salt is decomposed, water and sulphur are evolved, and a mixture of soda and sulphate of soda remains:—



The sulphite of soda dissolves readily in 4 parts of water, yielding an alkaline solution; it is most soluble at $91^\circ.4 \text{ F.}$ (33° C.)

Uses.—This salt is occasionally employed in analysis as a deoxidizing agent; it has lately become an article of commerce, being used, under the name of *antichlore*, to neutralize any excess of chlorine which may have been used in bleaching certain fabrics. The action of chlorine, in presence of water, upon sulphite of soda, will be understood from the following equation:—



Sulphite of soda has also been recommended for the preservation of wines, and for the refining of beetroot sugar.

A crystallizable *bisulphite of soda*, $\text{NaO.SO}_2, \text{HO.SO}_2$, has been obtained.

SULPHATE OF SODA, GLAUBER'S SALT, NaO.SO_3 .

§ 167. This salt, in the anhydrous state, sometimes forms an incrustation upon the surface of the soil; it is then called *Thénardite*; it also occurs in sea-water and in mineral waters.

Preparation.—Sulphate of soda is sometimes prepared from the mother-liquors of salt, extracted from salt-springs; these mother-liquors are exposed in the winter, when the decrease of temperature causes a crystallization of sulphate of soda.

A larger quantity of this salt, however, is prepared by decomposing chloride of sodium with sulphuric acid (*see p. 264*). It is also a by-product in the preparation of nitric acid on the large scale, and may be purified by dissolving to saturation in tepid water and crystallization.

Properties.—Sulphate of soda occurs in commerce in large transparent prismatic crystals, of the formula $\text{NaO.SO}_3 + 10\text{Aq}$; these effloresce in moderately dry air, becoming first covered with a white pulverulent crust, and afterwards falling to a white powder of anhydrous sulphate of soda, NaO.SO_3 . When heated to about 86° F. (30° C.), the crystals fuse in their water of crystallization; at a higher temperature, all the water is expelled, but the salt undergoes no further alteration. The crystals are insoluble in alcohol.

The solubility of crystallized sulphate of soda in water presents a strange ano-

¹ On the large scale, this salt is prepared by passing sulphurous acid over moist crystals of carbonate of soda; the sulphurous acid is evolved from burning sulphur, and the excess is sometimes passed into the leaden chambers in which oil of vitriol is prepared.

maly. Water at 91°.5 F. (33° C.) dissolves a larger quantity of this salt than at a higher or lower temperature; 1 part of the crystals dissolves, at 32° F. (0° C.), in 8.22 parts of water, at 77° F. (25° C.), in 1 part of water, and at 91°.5 F. (33° C.) in 0.31 part. A solution saturated at this last temperature, when heated to 212° F. (100° C.), deposits rhombic octohedra, which are anhydrous. If such a saturated solution be allowed to cool, it deposits four-sided prisms of the formula $\text{NaO.SO}_3 + 8\text{Aq}$, until the temperature has fallen to 68° F. (20° C.), after which crystals of the ordinary salt make their appearance.

If a saturated solution of sulphate of soda be covered with a layer of oil, and allowed to cool, it will remain without crystallizing until it is agitated, when it at once crystallizes throughout.

The crystals of anhydrous sulphate of soda absorb water from the air, and fall to a powder containing 8 equivalents of water; the anhydrous salt fuses at a red heat.

Uses.—Sulphate of soda is used to a considerable extent in medicine. It is very largely employed in the manufacture of carbonate of soda (§ 170). The sulphate of soda, in conjunction with common hydrochloric acid, is also used as a refrigerator in the ice-making machines, since such a mixture produces intense cold. For this purpose, 5 parts of common hydrochloric acid are poured upon 8 parts of crystallized sulphate of soda in coarse powder.

BISULPHATE OF SODA, $\text{NaO.SO}_3, \text{HO.SO}_3$.—This salt may be obtained by mixing a solution of sulphate of soda with 1 equivalent of sulphuric acid, and evaporating when crystals are deposited of the formula $\text{NaO.SO}_3, \text{HO.SO}_3 + 2\text{Aq}$. When heated, these undergo the aqueous fusion, and are converted into $\text{NaO.SO}_3, \text{HO.SO}_3$; if further heated, this latter loses the last equivalent of water, leaving NaO.2SO_3 , from which, at a higher temperature, one equivalent of SO_3 may be distilled,¹ the residue consisting of anhydrous sulphate of soda, NaO.SO_3 . The crystallized bisulphate does not deliquesce, but is very soluble in water; its solution has an acid reaction. A large quantity of water decomposes it into neutral sulphate of soda and free sulphuric acid.

If half an equivalent of sulphuric acid be added to one equivalent of sulphate of soda, a *sesquisulphate of soda* is said to be produced.

PHOSPHATES OF SODA.

§ 168. Soda forms a complete series of salts with the three modifications of phosphoric acid, viz:—

With the tribasic (common) phosphoric acid.

Triphosphate of soda	3NaO.PO_3
Common phosphate	2NaO.HO.PO_3
Acid phosphate	NaO.2HO.PO_3

With the bibasic (pyro-) phosphoric acid.

Dipyrophosphate of soda	2NaO.PO_3
Acid pyrophosphate	NaO.HO.PO_3

With the monobasic (meta-) phosphoric acid.

Metaphosphate of soda	NaO.PO_3
---------------------------------	-------------------

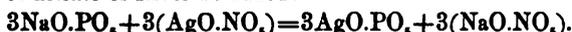
TRIPHOSPHATE (OR SUBPHOSPHATE) OF SODA. 3NaO.PO_3 .

This salt may be obtained by adding an excess of soda to a solution of the common phosphate, 2NaO.HO.PO_3 , and evaporating to crystallization. Six-sided

¹ Bisulphate of soda may be employed for the preparation of fuming sulphuric acid.

prisms are obtained, of the formula $3\text{NaO} \cdot \text{PO}_5 + 24\text{Aq}$. The crystals are unaltered in air, they undergo aqueous fusion below 212°F . (100°C .), and lose all their water at a red heat.¹ They are soluble in 5 parts of cold water, yielding an alkaline solution; an equivalent of soda is easily withdrawn from this solution, even by feeble acids; thus, if exposed to air, it absorbs carbonic acid, yielding carbonate and common phosphate of soda ($2\text{NaO} \cdot \text{HO} \cdot \text{PO}_5$).

With solution of nitrate of silver, triphosphate of soda gives a yellow precipitate of triphosphate of silver, $3\text{AgO} \cdot \text{PO}_5$, the supernatant liquid becoming neutral if an excess of nitrate of silver be added:—



COMMON PHOSPHATE OF SODA.



The common phosphate of soda occurs in the urine.

Preparation.—The solution of acid phosphate of lime which is obtained on decomposing bone-earth with sulphuric acid, as in the preparation of phosphorus, is mixed with solution of carbonate of soda, as long as any precipitate is produced; the lime is precipitated as a basic phosphate, together with phosphate of magnesia; the filtered liquid containing the phosphate of soda is evaporated, allowed to crystallize, and the salt subsequently purified by recrystallization.

Properties.—The ordinary phosphate of soda is thus obtained in transparent oblique rhombic prisms, of the formula $2\text{NaO} \cdot \text{HO} \cdot \text{PO}_5 + 24\text{Aq}$. These effloresce rapidly in air. When moderately heated, they undergo the aqueous fusion, and lose 24 eqs. of water, leaving a white mass of $2\text{NaO} \cdot \text{HO} \cdot \text{PO}_5$, and if this be redissolved in water, crystals of the original salt may be obtained from the solution; at a red heat, the equivalent of basic water is expelled, and $2\text{NaO} \cdot \text{PO}_5$ (pyrophosphate of soda) left; if the mass be now dissolved in water, the solution deposits no longer crystals of the original salt, but those of pyrophosphate of soda.

The crystals of common phosphate of soda dissolve in 4 parts of cold and 2 of hot water; the solution has an alkaline reaction, and is capable of absorbing carbonic acid (probably giving rise to $\text{NaO} \cdot \text{CO}_2$, and $\text{NaO} \cdot 2\text{HO} \cdot \text{PO}_5$); when the solution is kept in bottles of ordinary lead-glass, the latter is attacked, and white scales (phosphate of lead?) separate from it; the solution should therefore be preserved in German glass bottles, which are not corroded by it. When the solution of common phosphate of soda is evaporated at $91^\circ.5 \text{F}$. (33°C .), and left to crystallize, crystals are obtained of the formula $2\text{NaO} \cdot \text{HO} \cdot \text{PO}_5 + 14\text{Aq}$; these do not effloresce in air, and behave like the ordinary crystals when heated. Nitrate of silver produces, in solution of common phosphate of soda, a yellow precipitate of triphosphate of silver ($3\text{AgO} \cdot \text{PO}_5$), the supernatant liquid being acid:—



Hydrochloric acid removes half the soda from the common phosphate, converting it into acid phosphate of soda.

Uses.—Common phosphate of soda is administered medicinally as a purgative; it is employed in analysis (*see* Reagents), and is the source from which the other phosphates of soda are generally prepared.

ACID PHOSPHATE OF SODA, $\text{NaO} \cdot 2\text{HO} \cdot \text{PO}_5$, is obtained by adding tribasic phosphoric acid to solution of common phosphate of soda until it ceases to precipitate chloride of barium; the solution is then evaporated and left to crystal-

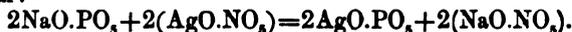
¹ Gerhardt states that this salt, dried at 212°F . (100°C .), has the formula $3\text{NaO} \cdot \text{PO}_5 + \text{HO}$. After the salt has been ignited, it absorbs 1 equivalent of water with remarkable avidity.

lize, when prismatic crystals¹ are obtained, of the formula $\text{NaO} \cdot 2\text{HO} \cdot \text{PO}_3 + 2\text{Aq}$; when these are heated to 212°F . (100°C .) the 2 eqs. of water of crystallization are expelled, and at about 392°F . (200°C .) a third equivalent of water is expelled, leaving $\text{NaO} \cdot \text{HO} \cdot \text{PO}_3$ (acid pyrophosphate of soda), which is converted into the metaphosphate ($\text{NaO} \cdot \text{PO}_3$) below 482°F . (250°C .) The acid phosphate of soda is easily soluble in water, and insoluble in alcohol; the aqueous solution is of course acid, and gives, with nitrate of silver, a yellow precipitate of triphosphate, the supernatant liquid being strongly acid:—



DIPYROPHOSPHATE, OR PYROPHOSPHATE OF SODA, $2\text{NaO} \cdot \text{PO}_3$.

This salt is obtained by heating the common phosphate of soda to redness, when it is left as a transparent glass. If this glass is dissolved in hot water, and the solution cooled, prismatic crystals are deposited, of the formula $2\text{NaO} \cdot \text{PO}_3 + 10\text{Aq}$; they do not effloresce in air. The aqueous solution of this salt has an alkaline reaction; when boiled, it is scarcely altered, but if previously acidulated, even with acetic acid, the salt $2\text{NaO} \cdot \text{HO} \cdot \text{PO}_3$ is obtained on boiling. A solution of pyrophosphate of soda is capable of dissolving several insoluble pyrophosphates, such as pyrophosphate of silver. The solution of pyrophosphate of soda gives a white precipitate with nitrate of silver, the supernatant liquid being neutral:—



ACID PYROPHOSPHATE OF SODA, $\text{NaO} \cdot \text{HO} \cdot \text{PO}_3$, may be obtained, as already stated, by heating the salt $\text{NaO} \cdot 2\text{HO} \cdot \text{PO}_3$ to about 392°F . (200°C .) It can be prepared also by dissolving pyrophosphate of soda ($2\text{NaO} \cdot \text{PO}_3$) in acetic acid, and adding alcohol, when the salt in question is precipitated, and acetate of soda remains in solution.

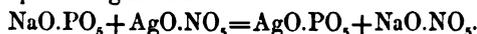
The acid pyrophosphate is obtained as a white crystalline powder, which, when heated, is converted into metaphosphate ($\text{NaO} \cdot \text{PO}_3$). The acid salt dissolves easily in water, and gives an acid solution, from which nitrate of silver throws down white pyrophosphate of silver ($2\text{AgO} \cdot \text{PO}_3$), the supernatant liquid being acid:—



The salt cannot be crystallized by evaporating its aqueous solution, but regular crystals have been obtained by pouring a layer of alcohol upon its surface, and allowing it to stand.²

METAPHOSPHATE OF SODA, $\text{NaO} \cdot \text{PO}_3$.

This compound may be easily prepared by expelling the water either from the acid tribasic phosphate, $\text{NaO} \cdot 2\text{HO} \cdot \text{PO}_3$, or from the acid pyrophosphate, $\text{NaO} \cdot \text{HO} \cdot \text{PO}_3$, or, more readily, by igniting microcosmic salt, $\text{NaO} \cdot \text{NH}_4 \cdot \text{O} \cdot \text{HO} \cdot \text{PO}_3$. It is left, after ignition, as a clear glass, which, if slowly cooled, is crystalline; it deliquesces in air, and dissolves very readily in water, but is insoluble in alcohol; its solution is almost neutral, and, if evaporated in a shallow vessel, at about 86°F . (30°C .), deposits, according to Fleitmann and Henneberg, oblique rhombic prisms, containing 4 eqs. of water. The aqueous solution gives, with nitrate of silver, a white precipitate of metaphosphate of silver ($\text{AgO} \cdot \text{PO}_3$), the supernatant liquid being neutral:—



¹ This salt may also be obtained in octohedra.

² A double pyrophosphate of potassa and soda ($\text{KO} \cdot \text{NaO} \cdot \text{PO}_3 + 12\text{Aq}$) is obtained by neutralizing the acid pyrophosphate of soda with carbonate of potassa, and evaporating to crystallization.

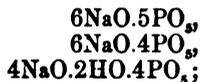
If the ignited metaphosphate of soda be rapidly cooled, its aqueous solution will not crystallize on evaporation. If the salt NaO.HO.PO_3 be heated until it has lost all its water, but has not fused, it dissolves with difficulty in water.

All the phosphates of soda, when fused with excess of hydrate or carbonate of soda, are converted into 3NaO.PO_3 .

Fleitmann and Henneberg, who have recently studied the phosphates of soda, are disposed to consider the metaphosphate as 6NaO.6PO_3 , and observed that if the composition of the other phosphates be referred to the same quantity of base, viz. 6 eqs., a series will be obtained in which certain *hiatus* exist, which these chemists have endeavored to fill up; thus:—

NaO.PO_3	will become	6NaO.6PO_3
NaO.HO.PO_3	“	3NaO.3HO.3PO_3
2NaO.PO_3	“	6NaO.3PO_3
NaO.2HO.PO_3	“	2NaO.4HO.2PO_3
2NaO.HO.PO_3	“	4NaO.2HO.2PO_3
3NaO.PO_3	“	6NaO.2PO_3

Of the members required to complete this series, Fleitmann and Henneberg believe that they have discovered three, viz:—



the two former having been obtained by fusing different mixtures of metaphosphate and pyrophosphate of soda, and the last compound by drying the acid pyrophosphate of soda (NaO.HO.PO_3) at 220°F .

CARBONATE OF SODA, commonly called SODA.



§ 169. Carbonate of soda occurs as a natural product in the *soda-lakes* of Egypt and Hungary; it also sometimes forms an incrustation on the soil in those countries; the walls of houses built with limestone containing much soda-salt are occasionally covered with an incrustation composed of carbonate mixed with sulphate of soda. This carbonate also exists in large quantity in the ashes of marine plants, being produced by the decomposition of salts of soda with organic acids, during incineration.

Preparation.—The old process for obtaining carbonate of soda, which is very little practised at the present day, consists in the incineration of various plants growing on the sea-shore, especially of the *salsola soda* and *salicornia Europaea*; the plants are collected, and burnt in trenches, when a grayish semi-fused as his obtained, which contains carbonate of soda mixed with various impurities, especially sand, carbon, salts of lime, sulphate, and hyposulphite of soda, sulphide and chloride of sodium. This product is introduced into commerce under the names *Barilla*, *Blanquette*, *Salicor*, and *Kelp*. Of these, the barilla, or Alicant soda, is said to be the richest, and the kelp, or Scotch soda, the poorest in carbonate of soda.¹ This product may be purified by lixiviation, and crystallization (see Manufacture of Nitre, § 145).

Previously to the French Revolution, in the latter part of the last century, a large quantity of the carbonate of soda consumed in France was imported from Spain; but during the war, the price of the barilla having risen very considerably, a premium was offered by the government for the discovery of a process

¹ Barilla contains from 25 to 80 per cent. of carbonate of soda, salicor, about 14 or 15; blanquette, 8 to 8; and kelp, only 2 per cent.

for the artificial production of carbonate of soda from some native source; such a process was discovered by Leblanc, and has been employed ever since without any essential alteration. This process for the artificial production of carbonate of soda merits a considerable share of our attention, since it has not only exerted a very important influence upon the various manufactures in which this salt is employed, *e. g.* those of soap and glass—and upon others which are called into play by the process itself, *e. g.* that of sulphuric acid—but has also very materially contributed to the general advancement of chemical science.

MANUFACTURE OF CARBONATE OF SODA FROM COMMON SALT.

§ 170. Leblanc's process for the preparation of carbonate of soda from chloride of sodium consists:—

1. In the conversion of chloride of sodium into sulphate of soda;
2. In the reduction of the sulphate of soda to sulphide of sodium by roasting with carbon; and
3. In the conversion of the sulphide thus obtained into carbonate of soda, by roasting with coal and limestone.

A charge of about 6 cwts. of chloride of sodium (ordinary sea-salt, or powdered rock-salt) is spread out on the floor of a reverberatory furnace,¹ and well mixed with an equal weight of oil of vitriol (spec. grav. 1.6), just as it is derived from the leaden chambers of the vitriol factory, which is usually in connection with the alkali works; these proportions leave the chloride of sodium slightly in excess. The mixture is then strongly heated by the coal-flame which plays over its surface, until it is converted into a perfectly dry mass of sulphate of soda, according to the equation:—



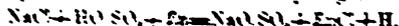
Very large quantities of hydrochloric acid, therefore, pass off in this operation; this acid, in most cases, is said not to repay the manufacturer for collecting it, and yet must not be allowed to contaminate the air in the neighborhood, since its effects upon vegetation are highly injurious. It is generally either carried into the upper strata of the atmosphere by a high chimney, or conducted through towers filled with lumps of coke or with flints, over which water is allowed to trickle in a contrary direction to the stream of gas; a solution of hydrochloric acid is thus obtained.²

In some works, binoxide of manganese is added to the mixture of chloride of sodium and oil of vitriol, so that, instead of hydrochloric acid, chlorine is evolved, which is devoted to the manufacture of bleaching-powder; the mass is very strongly heated, and then exhausted with water, when the sulphate of soda alone is dissolved.

The reduction of the sulphate of soda to sulphide of sodium, and conversion of

¹ The floor or *sole* of the furnace is commonly lined with lead for this process; the bricks used in constructing the furnace are such as are not easily acted upon by acid vapors. The hearth is usually divided by a partition of bricks, into two compartments, in one of which (lined with lead), more remote from the grate, the decomposition is effected, while in that nearest to the grate (lined with fire-brick) the whole of the hydrochloric acid is expelled, and the sulphate of soda fused.

² Limestone (carbonate of lime) has also been employed to absorb the hydrochloric acid, carbonic acid being then evolved. It has also been proposed to decompose the chloride of sodium with sulphuric acid in the presence of zinc, when sulphate of soda and chloride of zinc are produced, with evolution of hydrogen:—



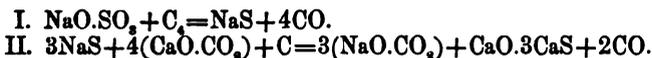
The products of the operation might be separated by crystallization, and the chloride of zinc afterwards decomposed by lime, when oxide of zinc would be obtained, which could be employed again to retain the hydrochloric acid.

this latter into carbonate of soda, are effected in one process, termed the *balling-process*¹ :—

100 parts of sulphate of soda,
103 parts of limestone,² and
62 parts of small coal,³

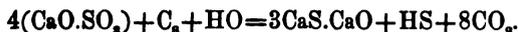
are well-ground, sifted, and very intimately mixed. This mixture, in charges of 3 or 4 cwts., is subjected to a gradually-increasing heat in a reverberatory furnace,⁴ and constantly stirred; during this operation, a blue flame of carbonic oxide is seen playing over the surface of the mass; as soon as the latter is in a state of tranquil fusion, the operation is completed; in practice, however, it is found advantageous to arrest the operation when there is still a lively disengagement of gas. The product thus obtained is termed *black ash*, and consists chiefly of a mixture of carbonate of soda with an insoluble oxysulphide of calcium, or of a combination of lime with sulphide of calcium.⁵

The decomposition which is effected in the balling-process will be readily understood from the following equations, the first representing the reduction of the sulphate of soda, the second the conversion of the sulphide of sodium into carbonate of soda :—



The proper regulation of the draught is of the greatest importance in the balling-process, so that a sufficiently high temperature may be obtained without introducing much free oxygen, which would oxidize the sulphides.

Some experiments of Unger's have recently shown that the presence of aqueous vapor must have a considerable influence upon the balling-process; for it was found that, when a mixture of gypsum and charcoal was exposed to the action of steam at a red heat, oxysulphide of calcium was formed, and hydrosulphuric acid evolved :—



Black ash, or crude soda, as it is sometimes termed, is used for some purposes in the arts. In this case it is prepared from sulphate of soda containing about $\frac{1}{2}$ of common salt, which causes the resulting soda-ash to crumble down in moist air, and renders grinding unnecessary. For the chief application of this product, viz. in soap-boiling, the presence of common salt is advantageous.

The black ash is now lixiviated with warm water,⁶ which dissolves out the carbonate of soda, forming a solution of a green color (apparently due to a little sulphide of iron), and leaves a residue consisting chiefly of the oxysulphide of

¹ So called because the ingredients accumulate into little round masses.

² The chalk or limestone should not contain much alumina. Deposits from carbonated waters are sometimes employed.

³ The coal must not leave too much ash.

⁴ This furnace has a double hearth; a melting hearth nearer to the grate, and somewhat lower than the more remote hearth, from which the dried materials are raked into the former hearth. Some furnaces have three hearths.

⁵ The composition of this compound, according to Dumas, is CaO.2CaS , according to Unger, CaO.3CaS .

⁶ In order to disintegrate the black ash, previously to lixiviation, it is sprinkled with water while hot, when it soon crumbles down. It is then inclosed in perforated boxes of sheet-iron, and suspended just below the surface of water, at a temperature of about 104°F. (40°C.), in the lixiviating cisterns, which are so arranged that the water shall come in contact, first with the nearly exhausted ash, afterwards with that which has lost some of its alkali to a former portion of water, and lastly, with the fresh ash; this is effected by placing the iron cases in each cistern in succession, beginning at the last, while the water is allowed to enter at the first cistern and to flow through to the last; the object being to economize both water (and consequently fuel) and alkali.

calcium and carbonate of lime.¹ This residue is known as *soda-waste*, and is occasionally used as a cement for rough building purposes. The lye containing the carbonate of soda is evaporated to dryness in iron pans, and the residue, which is termed *crude soda-ash*, is mixed with small coal or sawdust, and heated in a reverberatory furnace, when the sulphate and hydrate of soda which it contains are converted into carbonate; the salt is now redissolved in water, and the solution evaporated to crystallization, when large crystals of ordinary washing-soda are obtained.

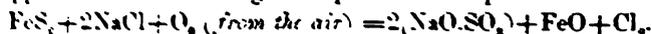
The following analysis of the products of the soda-manufacture have been made by Unger :—

	Black ash.	Soda-waste.
Sulphate of soda	1.99	
Carbonate "	23.57	
Hydrate "	11.12	
Chloride of sodium	2.54	
Sulphide "		1.78
Carbonate of lime	12.90	19.56
Sulphate "		3.69
Hyposulphite of lime		4.12
Hydrate "		10.69
Sulphide of calcium	34.76	3.25
Bisulphide "		4.67
Oxysulphide " (3CaS.CaO)		32.80
Silicate of magnesia	4.74	6.91
Sulphide of iron	2.45	
Oxide of iron		3.70
Charcoal	1.59	2.60
Sand	2.02	3.09
Water	2.10	3.45
	99.78	100.31

100 parts of sulphate of soda have been found to yield 153 to 168 parts of black ash, containing from 50 to 55 parts of carbonate of soda; theoretically, 75 parts of carbonate should be obtained.

In order to prepare perfectly pure carbonate of soda for chemical purposes, it may be converted into the bicarbonate (as described hereafter), the latter washed with cold water till the washings are free from chlorine and sulphuric acid, and then ignited, to reconvert it into carbonate.

According to a process recently patented, chloride of sodium is converted into sulphate of soda by roasting with iron-pyrites (FeS_2) in a reverberatory furnace, when it appears that the following decomposition takes place :—



The chlorine of course escapes, and the oxide of iron is converted, by further absorption of oxygen, into sesquioxide.

The sulphate of soda is extracted from the mass by water, or the mass may be subjected, at once, to the balling-process.

[Various other methods have been proposed for converting the common salt into sulphate of soda without the use of sulphuric acid: on boiling a solution containing chloride of sodium and sulphate of magnesia, a double decomposition ensues, resulting in the production of sulphate of soda and chloride of magnesium, which may be separated by crystallization; the latter salt may afterwards be pre-

¹ If only 1 eq. of limestone were used for each eq. of sulphate of soda, it would be found that, on treating the black ash with water, the decomposition would be reversed, sulphide of sodium and carbonate of lime being reproduced.

precipitated as carbonate, and reconverted into sulphate by means of sulphate of lime. Common salt may also be decomposed by sulphate of ammonia (obtained from gas or bone-black factories) or by sulphate of iron.

Dyer and Hemming have proposed to convert common salt directly into carbonate of soda by means of sesquicarbonate of ammonia. Tilghman's process consists in passing steam into an iron retort, in which chloride of sodium is maintained in a state of fusion; the steam thus takes up a considerable amount of vapor of chloride of sodium, and is then passed over lumps of alumina (prepared by igniting the sulphate) heated to redness in a cylinder of fire clay, *aluminate of soda* and hydrochloric acid are thus produced; the former is extracted by water and decomposed by carbonic acid, when carbonate of soda is obtained. This process, however, requires a very high temperature. The same author has described another method in which sulphate of soda is produced by the action of steam, at a high temperature, upon a mixture of common salt and gypsum (hydrochloric acid being evolved). The sulphate of soda is afterwards decomposed by the united agencies of alumina and steam, at a high temperature.]

The above brief description of Leblanc's process will suffice to show the great influence which it must have exerted upon various manufactures. When it is remembered that we have in this country practically inexhaustible supplies of chloride of sodium, of coal, and of limestone, and that the alkali produced from these ingredients may be converted, almost on the spot, into soap and glass, two materials for which there must be constantly a great demand, it will excite little surprise that this process should be looked upon as contributing, in no small degree, to the prosperity of the country, and the well-being of the community, especially since it will be seen to stand in intimate connection with the manufacture of bleaching-powder, with that of sulphuric acid, and through the latter, to produce an effect upon the numerous processes in which that acid is largely employed. It is, probably, no exaggeration to say, that the discovery of the artificial production of soda forms the most important epoch in the annals of chemical manufactures, and that it has given a greater impulse to the science of chemistry than any other of the numerous discoveries of recent times.

§ 171. PROPERTIES OF CARBONATE OF SODA.—This salt occurs in commerce in oblique rhombic prisms of the formula $\text{NaO.CO}_2 + 10\text{Aq}$; the water amounts to 62.9 per cent. These crystals effloresce rapidly in air; when heated, they fuse readily in their water of crystallization, and, if the heat be continued for a sufficient period, are converted into anhydrous carbonate of soda. The latter fuses at a moderate red heat, into a clear liquid, which is not affected by a higher temperature, and becomes crystalline on cooling.

The ordinary crystals dissolve in 2 parts of cold water, and in less than their own weight of boiling water, the solution is strongly alkaline, but not so caustic as that of carbonate of potassa. Tables will be found in larger chemical works for deducing the strength of a given solution from its specific gravity. If a hot saturated solution of this salt be allowed to cool, it deposits rectangular prisms of the formula $\text{NaO.CO}_2 + 8\text{Aq}$. Rhombic octohedra containing 5 eqs. of water of crystallization are formed, when the ordinary crystals effloresce in air at $54^\circ.5$ F. ($12^\circ.5$ C.), and are deposited at a temperature above $91^\circ.5$ F. (33° C.) from the ordinary salt when fused in its water of crystallization. If a saturated aqueous solution of carbonate of soda be evaporated between 77° and 99° F. (25° and 37° C.), four-sided tables are obtained, of the formula $\text{NaO.CO}_2 + \text{Aq}$. These crystals do not fuse when gently heated, and lose all their water at a temperature below the boiling-point. When exposed to air they absorb four more equivalents of water.

Carbonate of soda is sparingly soluble in alcohol.

When steam is passed over carbonate of soda at a bright red heat, hydrate of soda is formed, and carbonic acid disengaged.

Phosphorus at a high temperature reduces the carbonate, carbon being separated, and phosphate of soda formed.

Uses.—The uses of carbonate of soda are very numerous; we have already more than once alluded to its application in glass and soap-making; it is also constantly used in manufactures, merely as an alkali, for neutralizing acids, and is very largely employed for cleansing various fabrics. The chemist finds, in carbonate of soda, a source of many other soda-salts, especially of the bicarbonate, and makes use of it for precipitating the insoluble carbonates, for example, that of magnesia.

The specimens of carbonate of soda found in commerce differ very considerably in value, from the different amount of impurity which they contain; the chief of these impurities are hydrate of soda (produced by the decarbonation of the carbonate by the lime formed by the action of a high temperature upon the limestone), sulphate of soda, hyposulphite of soda, sulphide of sodium, sulphate of lime, carbonate of lime, alumina, and silica (for the method of detecting these see Analysis, Reagents).

For the method of ascertaining the amount of available alkali in carbonate of soda, we refer to Quantitative Analysis, Special Methods.

A double carbonate of potassa and soda, of the formula $2(\text{NaO} \cdot \text{CO}_2) + \text{KO} \cdot \text{CO}_2 + 18\text{Aq}$, has been crystallized from a mixture of solutions of these salts; it appears to be owing to the formation of a double carbonate, that a mixture of single equivalents of these two salts fuses much more readily than either of the salts separately.

§ 172. SESQUICARBONATE OF SODA, $2\text{NaO} \cdot 3\text{CO}_2$, occurs in the mineral kingdom as *Trona* and *Urao*, both which have the formula $2\text{NaO} \cdot 3\text{CO}_2 + 4\text{Aq}$. It may be prepared by rapidly boiling an aqueous solution of the bicarbonate, when the salt crystallizes out, on cooling, in prismatic crystals of the above formula. It is less soluble in water than the carbonate, but more so than the bicarbonate.

BICARBONATE OF SODA, $\text{NaO} \cdot \text{CO}_2 \cdot \text{HO} \cdot \text{CO}_2$.

This salt occurs in certain alkaline mineral waters.

Preparation.—It may be prepared by passing carbonic acid to saturation through a concentrated solution of the carbonate, when crystals of the bicarbonate are deposited; the same salt is obtained on the large scale by exposing the crystallized carbonate, in wooden boxes, to a current of carbonic acid, which is sometimes evolved from chalk by the hydrochloric acid flowing out of the condensers in the soda-manufacture.

The box containing the crystals is provided with a small pipe, through which the separated water of crystallization escapes. The absorption of the carbonic acid is attended with considerable evolution of heat. The bicarbonate is dried at a very gentle heat, and ground between stones, care being taken that the friction does not evolve sufficient heat to expel any carbonic acid.

It may also be prepared by stirring up 3 or 4 parts of crystallized carbonate of soda with 1 part of sesquicarbonate of ammonia, and exposing the mixture to the air till the ammonia has escaped. Again, if chloride of sodium be dissolved in three parts of water, and an equal weight of powdered sesquicarbonate of ammonia be added, crystals of bicarbonate of soda are deposited after some hours; in this case, the bicarbonate contained in the salt of ammonia is decomposed by the chloride of sodium.

Properties.—Bicarbonate of soda crystallizes in prisms of the formula $\text{NaO} \cdot \text{CO}_2 \cdot \text{HO} \cdot \text{CO}_2$. It occurs in commerce as a white crystalline powder. When exposed to air, it is gradually converted into sesquicarbonate, a change which may also be effected by gently heating; if a strong heat be applied, carbonate of soda alone remains.

Bicarbonate of soda is sparingly soluble in cold water, yielding a solution which is alkaline to litmus, but not to turmeric; if the solution be boiled, carbonic acid is expelled, sesquicarbonate of soda being produced at first, and ultimately the carbonate. The bicarbonate of soda is frequently employed in medicine, since its taste is far less unpleasant than that of the neutral salt.

Bicarbonate of soda is distinguished from the carbonate and sesquicarbonate, by its giving no precipitate with solutions of magnesia-salts.

§ 173. BORATE OF SODA, $\text{NaO} \cdot \text{BO}_3$, is obtained by fusing a mixture of single equivalents of baborate and carbonate of soda; if the fused mass be dissolved in water, it may be crystallized with 8 equivalents of water; this salt absorbs carbonic acid from the air, and is converted into a mixture of carbonate and baborate of soda.

BIBORATE OF SODA, BORAX, $\text{NaO} \cdot 2\text{BO}_3$.

This salt is found in certain lakes in Thibet, and occurs native in some parts of the East Indies, also in China, Persia, and Peru, whence it is imported under the name of *tincal*, which contains borax mixed with various saponaceous and other impurities. In order to *refine* tincal, it is repeatedly treated with lime-water, which removes a great portion of the soapy matter with which it is incrustated; the salt is then dissolved in hot water, and the solution mixed with a little chloride of calcium, when chloride of sodium is formed, together with an insoluble lime-soap; the clear liquid filtered from the latter, is evaporated to the proper extent, and set aside to crystallize in conical vessels of wood, lined with lead, the shape of which allows any insoluble matter to separate readily.

Another process consists in washing the tincal with a weak solution of soda, until the latter runs off colorless, when the soap is known to be washed away; the crystals are drained, dissolved in water, and a small quantity of soda added to the solution, to precipitate any earthy matters; the filtered liquid is afterwards evaporated to crystallization.

The larger quantity of the borax of commerce is prepared by dissolving 12 parts of crystallized carbonate of soda in 20 parts of water, and adding, in small portions, 10 parts of boracic acid;¹ the liquor is boiled, allowed to subside, and the clear portion decanted into leaden pans, where it is left to crystallize. The crystals which are then deposited are drained, redissolved in hot water, and allowed to crystallize by very slow cooling, since none but large crystals are marketable.

On this account, the liquor is allowed to crystallize in closed wooden cisterns, lined with lead, and inclosed in a wooden box, so that a space is left between the walls of the cistern and box, which is filled with some non-conducting substance (small coal, or woollen cloth), to prevent rapid cooling. The crystallization requires 25 to 30 hours. As much as possible of the mother-liquor is then rapidly drawn off with a siphon; and the rest is soaked up with sponges, so that no small crystals may be deposited; the case is then covered up, and the crystals allowed to cool slowly, so that they may not crack, after which they are sorted and packed.²

Two kinds of borax are found in commerce, *common borax*, $\text{NaO} \cdot 2\text{BO}_3 + 10\text{Aq}$, and *octohedral borax*, $\text{NaO} \cdot 2\text{BO}_3 + 5\text{Aq}$.

Octohedral borax is obtained by crystallization from a solution of spec. grav.

¹ If, as is sometimes the case, crude boracic acid (which contains about 8 per cent. of sulphate of ammonia) is employed for this purpose, the liquid is boiled, by the aid of steam, in a closed vessel, so that the carbonate of ammonia, which would otherwise be lost, may be conducted, by a tube, into sulphuric acid, and reconverted into sulphate.

² A process has been proposed for preparing borax in the dry way, by exposing, in thin layers, to a moderate heat (100° F.), a mixture of 88 parts of dry boracic acid, and 45 parts of crystallized carbonate of soda, when the carbonic acid is expelled.

1.166, which has been evaporated at 212° F. (100° C.). The deposition of octohedral borax begins at 174° F. (79° C.), and terminates at 133° F. (56° C.), when the mother-liquor must be rapidly removed, since ordinary borax begins to form. The octohedral borax forms very hard, compact plates of crystals. On account of a curious prejudice in the trade, the manufacturers are obliged to remove all projecting angles of the crystals before sending the octohedral borax into the market, since the appearance of such angles is supposed by the buyers to distinguish the ordinary borax.¹ The borax obtained from tincal does not decrepitate when heated, which causes it to be preferred, for soldering, to artificial borax. It is said, however, that by adding to the latter, previously to recrystallization, a small quantity of tincal, the disadvantage alluded to may be prevented.

Properties.—Common borax forms large transparent prisms, which effloresce when exposed to air; when heated, the crystals first decrepitate slightly, and undergo the aqueous fusion; they then lose their water, with very great intumescence, and form a white, spongy mass, which fuses at a red heat to a clear glass, unaltered at higher temperatures. The crystals of common borax dissolve in 12 parts of cold, and in 2 parts of boiling water; the solution has a feeble alkaline reaction.²

The crystals of octohedral borax become opaque in moist air, from absorption of water; they do not intumescence so violently when heated as those of ordinary borax.

The glass of borax, or *vitrified borax*, obtained, as above described, by heating the crystals, absorbs water from the air, and becomes opaque; in the fused state, it is capable of dissolving many metallic oxides, and is hence much used in blow-pipe experiments, and in assaying.

Uses.—Borax is extensively employed in the manufacture of some kinds of glass, in glazing stoneware, in smelting operations, and in soldering. In the last case, it serves to cleanse the surfaces of metal to be united from all oxide; the powdered crystals are sprinkled over the two surfaces, when they fuse on the application of the solder, and the fused borax is pressed out upon bringing the surfaces together. The octohedral borax is preferred for this purpose, because it intumescences less than the ordinary crystals.

The value of specimens of tincal is determined in the same way as that of carbonate of potassa, by adding the standard sulphuric acid to a solution of the salt, until the bright red color is produced in litmus; boracic acid, like carbonic, is capable of producing only a wine-red tint.

Another method (proposed by Schweitzer) consists in dissolving a weighed amount of the specimen in water, adding excess of hydrochloric acid, evaporating the solution to dryness, in order to expel the excess of hydrochloric acid, and determining the amount of chlorine existing in the residue (in the form of chloride of sodium), by precipitation, as chloride of silver (*see* Quantitative Analysis). One eq. (35.5 parts) of chlorine corresponds to 1 eq. (100.8 parts) of anhydrous borax.

Other acid borates of soda appear to exist, but are of no practical importance.

§ 174. We possess but little definite knowledge respecting the *compounds of silicic acid with soda*, which appear to be rather numerous; they may be obtained by fusing silica with different proportions of hydrate or carbonate of soda. Silicate of soda enters into the composition of most varieties of glass. The relations of soda to silicic acid are quite similar to those of potassa.

¹ A strange example of the inconvenience arising from a want of acquaintance with the first principles of chemistry.

² Schweitzer has shown, that when carbonic acid and sulphuretted hydrogen are passed, to saturation, into a strong aqueous solution of borax, the salt is completely decomposed.

PEROXIDE OF SODIUM, Na_2O_2 (?)

The composition of this oxide is uncertain; it is a greenish-yellow solid, which is obtained in the same way, and possesses the same properties in most respects, as the peroxide of potassium.

CHLORIDE OF SODIUM, COMMON OR CULINARY SALT, ROCK SALT, SEA SALT.
 NaCl .

§ 175. The conditions under which this salt is formed are exactly the same as those which furnish chloride of potassium; if sodium be heated to fusion in air, and then introduced into chlorine, it bursts out, after a few seconds, into a very vivid yellow flame, the jar becoming filled with thick white fumes of chloride of sodium.

Chloride of sodium is the most important salt contained in sea-water, in which it amounts to nearly 3 per cent.; various salt-springs are also very rich in this substance. Very extensive beds of rock salt are found in certain geological strata posterior to the coal formation, as may be seen at Northwich, in Cheshire, and in various parts of Spain and Poland. Large salt mines also exist in Mexico.

Preparation.—The rock salt of commerce is simply extracted from the salt-mines. It is then sometimes purified by dissolving in water, allowing the impurities to subside, and evaporating till crystals are deposited.

In warm situations (near Marseilles, for example), salt is obtained by the spontaneous evaporation of sea water in shallow pits dug in the sea-shore, and lined with clay; the salt forms a crust upon the surface, which is removed from time to time. The salt thus obtained is made into heaps and covered with straw, so as to protect it from the rain; the moisture of the atmosphere then causes the chloride of magnesium to deliquesce and drain off.

In Russia, the sea-water is allowed to remain in shallow pits till partly congealed; the ice, which retains very little salt, is removed, and the remaining brine evaporated.

Salt is also separated as a by-product in the evaporation of sea-water by artificial heat, on some parts of the coast of Britain, in order to obtain the sulphate of magnesia from the mother-liquor.

In some places, a reservoir of brine is made in the salt-beds by boring a hole, and introducing a quantity of water, which, when saturated with salt, is drawn off and evaporated.

At Droitwich, in Worcestershire, large quantities of salt are annually obtained from the salt-springs, the water of which is pumped up by steam-engines into iron pans, and evaporated by artificial heat.

In some parts of France and Germany, the water obtained from the salt-springs is not sufficiently concentrated to pay for evaporation by artificial heat. It is then partly evaporated, in the *graduating works*, by pumping it to the top of a wooden scaffolding, and allowing it to descend in the form of rain through a quantity of brush-wood and branches of trees, through which there is a strong current of air; in this way, a great part of the water is evaporated, and the brine becomes sufficiently strong for the salt pans. A brine containing only $1\frac{1}{2}$ per cent. of salt, may thus be concentrated to 18 per cent.¹

¹ These graduation-houses are erected in airy situations, and built at right angles to the direction of the prevailing wind. The operation proceeds best, of course, under the influence of a moderately warm, dry wind. Rain and frost are disadvantageous; the former for obvious reasons; the latter, because at temperatures below 27° F. (—3° C.), the sulphate of magnesia present in the brine decomposes the chloride of sodium, yielding sulphate of soda and chloride of magnesium, which interferes greatly with the subsequent crystallization.

After a little time, the brushwood and twigs become coated with an incrustation com-

The process by which the salt is extracted from the brines, is divided into two operations; the *schlotage*, or evaporation, and the *socage*, or crystallization. The brine is rapidly heated to violent ebullition, and fresh liquid continually added to replace the evaporated water. A considerable deposit is then formed, which consists chiefly of a double sulphate of soda and lime, and is removed from time to time. After about twenty-four hours, when a scum of crystallized salt begins to form on the surface, the temperature is allowed to fall considerably below the boiling-point of water, and maintained at that point for several days, while the crystallization is proceeding. The higher the temperature at which the crystals are deposited, the finer the grain of the salt. It is found that when chloride of magnesium is present in considerable quantity, a film of crystals of salt is continually formed upon the surface of the brine, and much retards the evaporation; this evil has been obviated by the addition of sulphate of soda, which converts the chloride of magnesium into sulphate of magnesia.¹

The crystals of salt are afterwards drained, dried by exposure to air, and packed.

The mother-liquors of the salt-works are employed for the preparation of sulphates of soda and magnesia, bromine and iodine.

Properties.—The ordinary rock-salt is usually contaminated with sesquioxide of iron, to which its peculiar rusty color is due. Perfectly pure rock-salt is transparent and colorless.² Its cleavage always exhibits the form of the cube. Common crystallized salt contains various impurities, consisting chiefly of sulphate of soda, chloride of calcium, sulphate of lime, chloride of magnesium, and sulphate of magnesia; the chlorides of calcium and magnesium confer upon it the property of becoming moist when exposed to air, which is not exhibited by pure salt.

Chloride of sodium crystallizes in cubes which are sometimes aggregated together in the form of hollow, four-sided pyramids; occasionally, it is deposited from urine in octohedra; the crystals contain no water of crystallization, and are generally transparent; they are unalterable in moderately dry air.

When heated, the crystals decrepitate, from the expansion of a little water mechanically inclosed: if heated to redness, they fuse to a clear liquid, which becomes crystalline on cooling; at a bright red heat, the salt volatilizes, unchanged, in thick white fumes. 1 part of chloride of sodium dissolves in about 2.7 parts of water; its solubility is very slightly increased by elevation of temperature. A saturated solution has a specific gravity of 1.205, and boils, according to Gay-Lussac, at 229°.5 F. (110° C.); if such a solution be exposed to a temperature of 14° F. (—10° C.), large transparent prisms are formed, of the composition $\text{NaCl} + 4\text{Aq}$. These crystals effloresce in the air at low temperatures, and are easily converted into the anhydrous cubical crystals. When a saturated solution of chloride of sodium is boiled in an open vessel, the ordinary cubical crystals are deposited. Chloride of sodium is almost insoluble in alcohol.

Uses of Chloride of Sodium.—Its use as a condiment suggests itself at once; again, its great antiseptic properties render it peculiarly applicable to the preservation of meat and other articles of food. The enormous consumption of chloride of sodium for the manufacture of carbonate of soda has already been mentioned.

posed chiefly of earthy carbonates, deposited in consequence of the escape of carbonic acid; this fills up the interstices in the heap, which is therefore changed every five or six years.

¹ Berthier has recommended hydrate of lime for the decomposition of the chloride of magnesium, when hydrate of magnesia is precipitated, and chloride of calcium remains in solution; on continuing the evaporation, the latter salt decomposes the sulphate of soda, yielding chloride of sodium, and sulphate of lime, which is deposited.

² Rose found, in the crystals of rock-salt from Wieliczka, a peculiar hydrocarbon (C_2H_6), which is confined in cavities in the salt, and escapes with a crackling noise on dissolving the crystals in water.

Chloride of sodium is also employed in glazing the coarser kinds of earthenware; for this purpose, it is thrown into the kiln in which such ware is baked, at a full red heat, when it is converted into vapor, which acts upon the surface of the clay in such a manner as to produce a silicate of soda, forming a true glass. Since the clay from which earthenware is fabricated almost invariably contains sesquioxide of iron, the decomposition may be represented by the following equation, where the clay is regarded as neutral silicate of alumina, containing sesquioxide of iron:—



The sesquichloride of iron is expelled in the state of vapor. If no sesquioxide of iron be present, nevertheless silicate of soda is formed, the aqueous vapor which is found amongst the products of combustion in the kiln taking part in the reaction, thus:—



The *bromide* and *iodide of sodium* crystallize in cubes which are very soluble in water; they are prepared in the same manner as the corresponding compounds of potassium, which they very much resemble. The iodide of sodium occurs, it will be remembered, in the mother-liquors of salt-works, &c.

The *fluoride of sodium* crystallizes in anhydrous cubes, which require 25 parts of water for solution.

SULPHIDES OF SODIUM.

§ 176. The sulphides of sodium are probably as numerous as those of potassium, but only the first of the series, NaS, appears to be well-known. This sulphide is obtained by methods exactly similar to those employed for the preparation of the sulphide of potassium, and crystallizes in large prismatic crystals, containing 9 eqs. of water. This compound resembles sulphide of potassium in all its properties; it is oxidized in the same manner when exposed to air, and also combines with the sulphur-acids.

By fusing together equal weights of carbonate of soda and sulphur, a liver of sulphur may be prepared, exactly similar to that obtained with carbonate of potassa, and sometimes used in medicine.

A *hydrosulphate of sulphide of sodium*, NaS.HS, is prepared by the same methods as the corresponding compound of potassium.

A sulphide of sodium appears to be an essential constituent of the color known as *ultramarine*. The natural ultramarine is extracted from the mineral known as *lapis lazuli*; it consists chiefly of silica, sulphuric acid, sulphur, alumina, soda, lime, and oxide of iron.¹

This pigment was first artificially prepared by Guimet, in 1827. The process by which it is obtained requires very great precaution to insure success, since the conditions necessary for the production of a perfect color are not thoroughly understood; every manufacturer has his own prescription for its preparation, but

¹ The following are the results of an analysis of lapis lazuli:—

Silica	45.40
Alumina	81.67
Soda	9.09
Sulphuric acid	5.89
Sulphur	0.95
Iron	0.86
Lime	8.52
Chlorine	0.42
Water	0.12
	97.92

This mineral is usually accompanied by iron-pyrites.

the essential part of the process appears to be the fusion, at a high temperature, of a mixture of soda, or carbonate of soda, sulphur, silica, and clay containing a little iron, and the subsequent roasting of the mass thus obtained. The product is washed with water, and dried. It is yet doubtful whether the presence of iron is essential (as is generally asserted) to the production of a blue color.

Ultramarine is very stable in the air; it resists the action of alkalis, and of a high temperature; acids, however, bleach it immediately, with evolution of sulphuretted hydrogen, showing that the sulphide which is present is essential to the color. If carbonate of potassa be substituted for carbonate of soda in the preparation of artificial ultramarine, a white compound is obtained, so that sodium would appear to be a necessary constituent.

Green ultramarine is said to consist of blue ultramarine which has not been roasted.

LITHIUM.

Sym. Li. Eq. 6.5.

§ 177. This somewhat rare metal was discovered in 1818, by Arfwedson. Its name is derived from *λίθος*, stony, because it was first obtained from a mineral.¹

Davy prepared lithium from the oxide, lithia, by means of the galvanic battery. Hitherto this metal has been obtained only in small quantity, but it is probable that larger quantities of it might be prepared by methods similar to those in use for extracting potassium and sodium from their oxides.

Lithium is very similar to potassium and sodium, and, like these metals, decomposes water at the ordinary temperature.

The OXIDE OF LITHIUM, LITHIA (LiO), occurs in certain minerals, particularly in spodumene, petalite, and lepidolite. The last is generally employed for the preparation of lithia; the powdered mineral is mixed with two parts of quicklime, and strongly heated; the mass is reduced to powder, and boiled with milk of lime, when alumina, sesquioxide of iron, and silica, are left undissolved, whilst the filtered solution contains potassa, soda, lithia, and a little lime; this solution is acidulated with hydrochloric acid, and concentrated, in order that most of the chloride of potassium may crystallize out; the lime is precipitated from the solution by carbonate of ammonia, the filtered liquid evaporated to dryness, and the residue ignited, to expel ammoniacal salts; this residue, consisting of the chlorides of potassium, sodium, and lithium, is digested with alcohol, which dissolves the chloride of lithium; this latter, after the evaporation of the alcohol, is decomposed by sulphuric acid, and the sulphate of lithia thus obtained subsequently converted into acetate by double decomposition with acetate of baryta; the solution of acetate of lithia, filtered from the sulphate of baryta, is evaporated to dryness, and the residue ignited, when it is converted into carbonate of lithia, from which hydrate of lithia may be obtained by decomposition with hydrate of lime.

Properties.—*Hydrate of Lithia* (LiO.HO) resembles in its properties the hydrates of potassa and soda, but is less soluble in water, and does not deliquesce in air.

Its solution has a strongly alkaline reaction, and its basic properties are very

¹ The chief minerals from which lithium is obtained are *lithion-spodumene* ($3(\text{LiO}.\text{SiO}_2)$), $4(\text{Al}_2\text{O}_3, 3\text{SiO}_2)$; *petalite* (silicate of soda, lithia, and alumina), and *lepidolite* or *lithia-mica* (containing silicates of alumina and lithia and silicofluoride of potassium).

powerful. Hydrate of lithia possesses the peculiar property of readily attacking platinum at a high temperature.

The *Salts of Lithia* are colorless, and much resemble those of potassa and soda; the *nitrate* is very soluble and deliquescent; the *sulphate* is soluble, and may be obtained in fine crystals; the *carbonate* is rather sparingly soluble; its solution has an alkaline reaction.

Phosphate of Lithia is sparingly soluble in water, and the *double phosphate of lithia and soda* is almost insoluble, so that we may test for lithia by mixing its solution with phosphate of soda, evaporating to dryness, and extracting with water, when the double phosphate of lithia and soda remains undissolved.

Chloride of Lithium crystallizes in cubes of the formula $\text{LiCl} + 4\text{Aq}$; it is deliquescent, and very soluble in water; it also dissolves readily in alcohol, therein differing from the chlorides of potassium and sodium.

The salts of lithia, when exposed on platinum wire to the inner blowpipe-flame impart a red color to the outer flame.

From the foregoing brief description of the characters of the salts of lithia, it will be seen that this oxide forms a sort of connecting link between the alkalies and alkaline earths.

AMMONIUM.

$\text{NH}_3 = \text{Am.}$ Eq. 18.

§ 178. This metal has never yet been obtained in the separate state; it is strictly hypothetical, and the grounds upon which its existence is assumed have been stated in the description of the compounds of nitrogen and hydrogen. The method by which the so-called *amalgam of ammonium* is prepared, together with the properties of this amalgam, have been detailed in the same place (§ 91).

Since the compounds produced by the combination of ammonium with the electro-negative elements, and of oxide of ammonium with the oxygen-acids, are very analogous to those formed by potassium and sodium, we have deferred the history of these compounds till the present occasion.

OXIDE OF AMMONIUM, $\text{NH}_3\text{O} = \text{AmO}$. Eq. 26.

A very good reason for supposing this compound to exist, although it has not been isolated, is found in the complete analogy between the salts, which are formed when ammonia (NH_3) is brought into contact with hydrated acids, and the corresponding salts of potassa and soda. When liberated from its compounds, oxide of ammonium is decomposed into ammonia and water.

NITRITE OF OXIDE OF AMMONIUM, NITRITE OF AMMONIA.

$\text{NH}_3\text{O}.\text{NO}_2 = \text{AmO}.\text{NO}_2$.

§ 179. This salt is prepared by decomposing nitrite of silver with chloride of ammonium, filtering from the precipitated chloride of silver, and evaporating the filtrate *in vacuo*; it may likewise be obtained by passing nitrous acid into excess of ammonia, and evaporating over lime. It forms a mass of confused crystals, which are easily decomposed by heat; they are very soluble in water, and the solution, like the solid, evolves nitrogen when heated, according to the equation:—

$\text{NH}_3\text{O}.\text{NO}_2 = 4\text{HO} + \text{N}_2$.

According to Millon, if the solution be rendered slightly alkaline by ammonia, this decomposition will be gradual, but if a slight excess of a mineral acid be

added, it will take place very rapidly. Concentrated sulphuric acid effects the same decomposition.

This salt is sometimes employed for the preparation of nitrogen (§ 80).

NITRATE OF OXIDE OF AMMONIUM, NITRATE OF AMMONIA.



The nitrate is prepared by dissolving ordinary sesquicarbonate of ammonia in moderately dilute nitric acid, perfectly free from hydrochloric acid, till the carbonate is slightly in excess; the solution is then evaporated down, till a drop placed upon a watch-glass solidifies on cooling, when the whole is poured out upon a clean stone slab, broken up, and preserved in a stoppered bottle.

If the evaporation be arrested at an earlier period, distinct crystals may be obtained on cooling, which are six-sided prisms, of the formula $\text{NH}_4\text{O.NO}_3 + \text{Aq}$.

Properties.—Nitrate of ammonia deliquesces on exposure to air, and is very soluble in water, with great reduction of temperature. When heated, it fuses at about 226° F. (108° C.), and at 482° F. (250° C.) is rapidly decomposed into water and oxide of nitrogen:—



If the temperature be raised so high that the vessel becomes filled with white fumes, there are produced, beside the oxides of nitrogen, a quantity of nitric oxide, free ammonia, and nitrite of ammonia. In the presence of spongy platinum, the salt is decomposed at 320° F. (160° C.), yielding water, nitric acid, and nitrogen:—

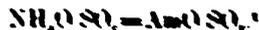


This salt deflagrates violently with carbon, and other combustible bodies, at a high temperature. When thrown into a red-hot crucible, it deflagrates, emitting a pale yellow light, probably due to a combustion of the ammonia at the expense of the nitric acid. When heated with an excess of concentrated sulphuric acid, nitrate of ammonia is decomposed in the same manner as when heated alone.

Nitrate of ammonia is employed as a source of nitrous oxide, and is also occasionally used to facilitate the incineration of organic substances, and in the preparation of refrigerating mixtures.

§ 180. SULPHITE OF OXIDE OF AMMONIUM, SULPHITE OF AMMONIA, $\text{NH}_4\text{O.S(O)}_2 = \text{Am(O.S(O)}_2)$.—When sulphurous acid is passed through an aqueous solution of ammonia, combination takes place, with disengagement of heat. The sulphite may be crystallised from this solution. It is very soluble in water; the solution evolves ammonia when boiled; the crystals, when heated, evolve ammonia and water, whilst a disulphite sublimes. The solution of sulphite of ammonia, prepared by passing sulphurous acid into solution of ammonia, is sometimes employed in analysis.

SULPHATE OF OXIDE OF AMMONIUM, SULPHATE OF AMMONIA.



Sulphate of ammonia occurs native as *rock-sulphate*, which is an efflorescence upon several lavas.

A class of substances which compounds of ammonia NH_3 in combination with certain sulphuric acids. (To avoid confusion with the compound NH_4SO_4 sulphate of ammonium) is a sulphate and NH_4SO_3 sulphite of ammonia, sometimes improperly termed sulphamate. These compounds are converted into the corresponding ammoniacal salts, when heated with water. The ammonia property is retained in compounds of amidogen (NH_2) with an acid, whose decomposition is effected, and may also be produced by the elimination of 5 equivalents of water from the ammoniacal salt. They are converted into salts in which the ammoniacal is being a white deliquescent.

Preparation.—This salt is prepared on a large scale from the ammoniacal liquors obtained in the destructive distillation of coal and bones; these contain ammonia chiefly in the form of carbonate; they are decomposed either by sulphuric acid or by sulphate of lime, in the former case, with evolution of carbonic acid, in the latter, with precipitation of carbonate of lime; the liquid containing the sulphate of ammonia is then evaporated to crystallization; the crystals thus obtained are gently heated, to destroy various organic matters with which they are contaminated, and are then recrystallized.

Properties.—Sulphate of ammonia is isomorphous with sulphate of potassa, crystallizing in flattened six-sided prisms, which contain no water of crystallization; it becomes slightly moist when exposed to air. When heated, the crystals decrepitate, afterwards fuse, and finally disappear entirely, sulphite of ammonia subliming, and water, ammonia, nitrogen, and sulphurous acid, passing off.

Sulphate of ammonia dissolves in 2 parts of cold and 1 part of boiling water. It has lately been proposed to employ this salt in order to render certain fabrics less combustible; it is also employed in the manufacture of artificial manures, and for the preparation of ammonia, alum, and other ammoniacal salts.

Bisulphate of Ammonia ($\text{NH}_4\text{O.SO}_3, \text{HO.SO}_3$) may be obtained by the addition of sulphuric acid to the neutral salt.

§ 181. The *Phosphates of Oxides of Ammonium* possess but little practical interest; when heated, they disengage ammonia and water, leaving phosphoric acid. Gay-Lussac has proposed the use of phosphate of ammonia for rendering stuffs incombustible.

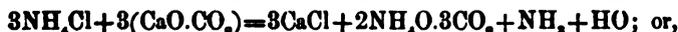
PHOSPHATE OF SODA AND AMMONIA, PHOSPHORUS SALT, MICROCOSMIC SALT.



This salt occurs in the urine. It is prepared by dissolving 6 or 7 parts of phosphate of soda (2NaO.HO.PO_3) and 1 part of chloride of ammonium in hot water, and allowing the solution to crystallize. It forms large transparent prisms, of the formula $\text{NaO.NH}_4\text{O.HO.PO}_3 + 8\text{Aq}$. The crystals effloresce slightly in air, and evolve a little ammonia. When gently heated, they fuse easily, and lose, at first, water and ammonia, being converted into NaO.HO.PO_3 ; if this last be further heated, it is, of course, converted into NaO.PO_3 . Microcosmic salt is easily soluble in water; the solution evolves ammonia when evaporated. This salt is much used as a flux in blowpipe experiments.

SESQUICARBONATE OF AMMONIA, SAL VOLATILE, COMMERCIAL CARBONATE OF AMMONIA, $2\text{NH}_4\text{O.3CO}_2$.

§ 182. This compound has been alluded to above, as produced in the destructive distillation of coal and bones; when obtained from these sources, it is generally purified by one or two sublimations with animal charcoal, which retains the empyreumatic matters; the ordinary process, however, by which the sesquicarbonate of commerce is prepared, consists in subliming a mixture of sulphate of ammonia (or chloride of ammonium) and 2 parts of chalk, in an earthen or iron retort, furnished with a receiver of earthenware or lead; the salt distils over in the liquid form, and solidifies in the receiver, which is broken up when the mass is removed. The decomposition is represented by the following equation:—



cent solid, produced by the action of dry ammonia upon *chlorosulphuric acid* (SO_2Cl), which is obtained when a mixture of chlorine and sulphurous acid is exposed to the action of solar light. *Phosphamide*, see § 116. *Carbamide* (NH_2CO) is obtained when ammonia acts upon chlorocarbonic acid gas.

The salt obtained by this process, however, is a mixture consisting chiefly of the sesquicarbonate with varying proportions of other carbonates.

Properties.—When freshly prepared, sesquicarbonate of ammonia forms a transparent fibrous mass, which, when exposed to air, soon becomes covered with an opaque, friable crust, into which the whole mass is gradually converted, the salt, meanwhile, exhaling a powerful odor of ammonia. This white crust consists of the bicarbonate of ammonia, and appears to be formed from the sesquicarbonate by the abstraction of ammonia and carbonic acid:—



This change takes place much more rapidly if the salt be powdered; when it is completed, the residue has lost its pungent odor. When sesquicarbonate of ammonia is heated, carbonic acid is evolved at first, and part of the sesquicarbonate of ammonia sublimes unchanged, whilst the remainder enters into fusion, and is decomposed into compounds containing different proportions of ammonia and carbonic acid. The sesquicarbonate of ammonia dissolves in about 3 parts of cold water; if the salt be treated with a small quantity of water, it appears to suffer a partial decomposition, the solution containing chiefly the neutral carbonate, $\text{NH}_4\text{O} \cdot \text{CO}_2$, and the residue the bicarbonate. If a warm saturated solution be allowed to cool, large crystals of bicarbonate of ammonia are deposited. The latter salt also appears to be precipitated when the aqueous solution of the sesquicarbonate is mixed with alcohol.

The aqueous solution has an alkaline reaction, and an ammoniacal odor; if exposed to the air, it is gradually converted into solution of the bicarbonate; when the solution is boiled, carbonic acid, and traces of ammonia, are disengaged with effervescence, and the neutral carbonate remains in solution; if this be further evaporated, the latter salt is also volatilized.

The *Bicarbonate of Ammonia*¹ may be obtained by passing carbonic acid through a concentrated solution of the sesquicarbonate; it is deposited in crystals of the formula $\text{NH}_4\text{O} \cdot \text{CO}_2 \cdot \text{HO} \cdot \text{CO}_2$, which have the same form as those of bicarbonate of potassa. They are inodorous, permanent in the air, and volatilize when heated; this salt is much less soluble in water than the neutral carbonate. When the solution is boiled, it disengages carbonic acid, and neutral carbonate of ammonia ($\text{NH}_4\text{O} \cdot \text{CO}_2$) remains in solution.

When sesquicarbonate of ammonia is dissolved in boiling water, in a flask, which is afterwards closed to prevent the escape of carbonic acid, the solution deposits, on cooling, large prismatic crystals of the formula $2(\text{NH}_4\text{O} \cdot \text{HO} \cdot 2\text{CO}_2) + \text{Aq}$.

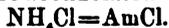
Sesquicarbonate of ammonia is employed as a smelling-salt, and, to a considerable extent, medicinally.

In the laboratory it is very useful as a reagent, and as a source of many other ammoniacal salts.

Other carbonates of ammonia, of more complicated composition, have been obtained, but present no points of interest.

The *Borates of Ammonia* are devoid of practical interest.

CHLORIDE OF AMMONIUM, HYDROCHLORATE OF AMMONIA, SAL-AMMONIAC.



§ 183. This salt is formed, in thick white fumes, when hydrochloric acid gas and ammoniacal gas are brought into contact; it is sometimes found in the neighborhood of volcanoes.

¹ If an aqueous solution of sesquicarbonate of ammonia be exposed to a temperature approaching the freezing point, it deposits crystals of the formula $2\text{NH}_4\text{O} \cdot 3\text{CO}_2 + 3\text{Aq}$.

² Bicarbonate of ammonia has been found in considerable quantity, forming crystalline masses, in a bed of guano on the western coast of Patagonia.

Preparation.—Chloride of ammonium was formerly prepared chiefly in Egypt, where the inhabitants collected the soot arising from the imperfect combustion of the dung of camels; this soot was afterwards heated in large glass flasks, when the chloride of ammonium sublimed in the upper part, and was extracted by breaking the flask.⁴

A large quantity of sal-ammoniac is now prepared from the ammoniacal liquors obtained in the distillation of bones for the preparation of animal charcoal, and of coal in the gas-works. These ammoniacal liquors are neutralized with hydrochloric acid (which decomposes the carbonate of ammonia and sulphide of ammonium, with evolution of carbonic and hydrosulphuric acids), evaporated, and allowed to crystallize; the salt is then gently heated to destroy the tarry matter which it contains, dissolved in water, and purified by animal charcoal; the pure crystals are afterwards sublimed in large earthen bottles, or in iron vessels, lined with clay, and provided with leaden domes.

Chloride of ammonium is also prepared by subliming a mixture of sulphate of ammonia and chloride of sodium, when



The sulphate of ammonia is obtained from the ammoniacal liquor of the gas-works, or of the bone-black factories, either by neutralizing them with sulphuric acid, or by double decomposition with a sulphate (of lime or oxide of iron).

The chloride of ammonium is also sometimes prepared from mixed solutions of sulphate of ammonia and chloride of sodium; on evaporation, the chloride of ammonium crystallizes out, and sulphate of soda remains in the mother-liquor.

Properties.—The sublimed chloride of ammonium of commerce forms a very tough, translucent, fibrous mass, generally retaining the shape of the vessel into which it was sublimed, and often of a brown color where it has been in contact with this vessel. It is not altered by exposure to air. At a red-heat it volatilizes in thick white clouds, without previously fusing. It may, however, be fused in a tube, which is hermetically sealed.

Chloride of ammonium dissolves in 2.7 parts of cold water, and in an equal weight of boiling water. The solution, on cooling, deposits anhydrous crystals of a peculiar feathery appearance and consisting of an assemblage of minute octohedra.

When an aqueous solution of chloride of ammonium is evaporated, a little of the salt passes off with the vapor.

The solution of chloride of ammonium is capable of dissolving many metallic oxides and salts insoluble in water. Chloride of ammonium is sparingly soluble in alcohol.

Many metals, at somewhat elevated temperatures, decompose chloride of ammonium, metallic chlorides being formed, while ammonia and hydrogen are evolved.

Uses of Chloride of Ammonium.—This salt is the source from which ammonia is always prepared in the laboratory, and is also very useful in analysis.

It is employed occasionally in soldering, to cleanse the metallic surfaces to be united; its action in this case appears to depend upon the principle which Rose has recently turned to account in analytical operations.

Rose found that when the arseniates, arsenites, antimoniates, and stannates of the alkalis were heated with several times their weight of chloride of ammonium, the arsenic, antimony and tin were volatilized in the form of chlorides. The alkaline phosphates were entirely converted into chlorides by the same treatment. Alumina was partly, and sulphate of alumina entirely, volatilized when heated

⁴ At Liège, sal-ammoniac is prepared by burning, in peculiarly constructed ovens, a mixture of coal, common salt, clay, and animal matter, collecting the soot, and separating the chloride of ammonium from it by sublimation.

with sal-ammoniac. Sesquioxide of iron was also partly volatilized. The oxides of nickel, cobalt, and bismuth, were reduced to the metallic state. Oxide of zinc, oxide of lead, sulphide of lead, and sulphate of zinc, were completely volatilized. These reactions have been applied by their discoverer to facilitate the quantitative analysis of various substances.

Chloride of ammonium is also employed in medicine.

The *bromide* (NH_4Br) and the *iodide* (NH_4I) of ammonium, much resemble the chloride.

SULPHIDE OF AMMONIUM, HYDROSULPHATE OF AMMONIA.



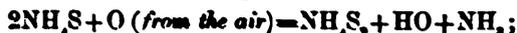
§ 184. This compound is obtained when hydrosulphuric acid gas is mixed with excess of ammoniacal gas in a vessel which is cooled down to 0° F. (-18° C.); it may also be obtained by distilling a mixture of single equivalents of chloride of ammonium and sulphide of potassium, the receiver being cooled to the above temperature.

When thus prepared, it forms colorless crystals, which decompose at the ordinary temperature, into ammonia and hydrosulphate of sulphide of ammonium:—



A solution of sulphide of ammonium is prepared by saturating a solution of ammonia with hydrosulphuric acid, and afterwards adding a quantity of the same solution equal to that originally employed; hydrosulphate of sulphide of ammonium ($\text{NH}_4\text{S.HS}$) is first produced, and is converted into sulphide of ammonium (NH_4S) by the additional equivalent of ammonia.

Properties.—The solution thus obtained, which is frequently employed in analysis, is colorless, possesses a strongly alkaline reaction, and a disagreeable odor of ammonia and hydrosulphuric acid. When exposed to air, it soon becomes yellow, from the formation of the *bisulphide*:—



a small quantity of hyposulphite of ammonia is also formed:—



A solution of pure sulphide of ammonium remains clear when mixed with excess of acid, whilst, if one of the higher sulphides be present, sulphur is deposited.

Sulphide of ammonium is a sulphur-base, like the sulphides of potassium and sodium; it hence dissolves the sulphides of arsenic, antimony, and other sulphur-acids.

The *Hydrosulphate of Sulphide of Ammonium* ($\text{NH}_4\text{S.HS}$), may be obtained, by passing equal volumes of ammonia and hydrosulphuric acid into a vessel surrounded with ice; it forms colorless needles, which are very volatile and soon decomposed in the air. Its solution is alkaline to test-papers.

Bisulphide of ammonium (NH_4S_2) is obtained in yellow crystals when vapors of sulphur and sal-ammoniac are passed through a porcelain tube, heated to redness, and connected with a cooled receiver.

It is very deliquescent, and is readily decomposed by acids, sulphuretted hydrogen being evolved, and sulphur deposited.

The compounds NH_4S_3 , NH_4S_4 , NH_4S_5 , and NH_4S_6 have been obtained.

The solution known as *Liquor Sulfureus Pyriticus*, is obtained by distilling a mixture of 1 part of sulphur with 2 parts of chloride of ammonium, and 2 or 3

¹ At ordinary temperatures, or when an excess of hydrosulphuric acid is employed, the compound $\text{NH}_4\text{S.HS}$ is obtained.

parts of lime; it appears to be a mixture of different sulphides of ammonium, especially of NH_4S and NH_4S_2 , with water. The reaction by which it is produced may probably be thus expressed:—



The liquid is obtained, even when the ingredients are anhydrous, in which case, water must be formed by a secondary decomposition between the lime and chloride of ammonium.

It is of a yellow color and disagreeable odor; it fumes in the air. *Liquor fumans Boylii* is sometimes, though rarely, used in medicine.

METALS OF THE SECOND GROUP.

(Metals of the Alkaline Earths.)

BARIUM.

Sym. Ba. *Eq.* 68.5.

§ 185. THIS metal was first obtained by Davy, in 1808. Its name is derived from βαρύς, heavy, because of the great density of its compounds. Barium occurs in considerable quantities in the mineral kingdom, in combination with oxygen and acids. Carbonate of baryta constitutes the mineral *witherite*, the sulphate is known as heavy spar.

Preparation.—Barium may be obtained by decomposing hydrate, carbonate, or nitrate of baryta, or chloride of barium, in a moist state, by the galvanic battery, in contact with mercury, into which the negative pole dips; an amalgam of barium is thus obtained, from which the mercury may be separated by distillation in an atmosphere free from oxygen.

Another method of preparing barium consists in passing the vapor of potassium over redhot baryta, in an iron tube, and extracting the barium from the resulting mixture of this metal with potassa, by means of mercury.

Small quantities of this metal may also be obtained by the reduction of baryta, supported on a piece of charcoal or slate, by a jet of a mixture of three volumes of hydrogen and one volume of oxygen, when globules of barium are obtained.

Properties.—Barium is a white malleable metal, not very lustrous. Its specific gravity is about 4. It fuses below a red heat, and volatilizes at a much higher temperature. When exposed to air, it becomes covered with a white coating of baryta; if heated in air, this oxidation is attended with combustion—Barium decomposes water energetically at common temperatures, hydrogen being evolved and baryta dissolved in the water.

BARIUM AND OXYGEN.

Baryta	BaO.
Binoxide of barium	BaO ₂ .

OXIDE OF BARIUM, BARYTA.

BaO. *Eq.* 76.5.

§ 186. Baryta is prepared by heating the nitrate of baryta to bright redness in a covered porcelain crucible or retort until no more fumes are evolved:—



It may also be obtained by reducing the carbonate of baryta, by means of charcoal, at a high temperature.

Baryta which has been prepared by igniting the nitrate in a porcelain or earthen vessel, generally contains certain earthy impurities; it is therefore better to heat the nitrate in a clean iron vessel; platinum should not be used, since it is easily attacked by baryta at a high temperature.

The crucible or retort employed in preparing baryta should be rather capacious, since the nitrate swells up very much when heated; for the same reason, the heat should be applied gradually.

Properties.—Baryta, thus obtained, is a gray, porous mass, which fuses only at a very high temperature; it is very heavy, having a specific gravity between 4 and 5. When exposed to air, it absorbs water, and falls to a white powder of hydrate of baryta; the same combination takes place, with great evolution of heat, when baryta is moistened with water.

HYDRATE OF BARYTA, BaO.HO.

In order to prepare the hydrate of baryta, a solution of sulphide of barium may be boiled with oxide of copper till it gives a white precipitate with acetate of lead; the solution is then rapidly filtered, evaporated, and the hydrate of baryta allowed to crystallize out; the following equation expresses the decomposition:—



Properties.—The crystals are transparent four or six-sided prisms, of the formula BaO.HO+9Aq. When exposed to air, they absorb carbonic acid, and are converted into carbonate of baryta; at a gentle heat, they lose the 9Aq, leaving pure hydrate of baryta, from which the water cannot be expelled by heat.

Hydrate of baryta fuses somewhat below redness, and becomes crystalline on cooling.

It is soluble in 2 parts of boiling, and 20 parts of cold water; the solution is strongly alkaline, and, if exposed to air, rapidly absorbs carbonic acid, and deposits carbonate of baryta. A cold saturated solution is known as *baryta-water*.

The hydrate, and all the soluble salts of baryta, are powerful poisons.

Hydrate of baryta is much employed in analysis.

The salts of baryta are, for the most part, neutral to test-papers.

NITRATE OF BARYTA, BaO.NO₃.

§ 187. This salt is prepared by dissolving carbonate of baryta in very dilute nitric acid, or by decomposing a dilute solution of sulphide of barium with this acid, evaporating and crystallizing.

Properties.—The nitrate forms white translucent octohedra, which are anhydrous, and unalterable in the air. When heated, they decrepitate, fuse easily, and are decomposed at a red heat, evolving peroxide of nitrogen (NO₂) and oxygen, and leaving a mass of baryta, which is much swollen from the escape of gas during the decomposition. If the heat be cautiously applied, *nitrite of baryta* is at first formed. The nitrate detonates, but not very violently, with combustible matters. It is soluble in 8 parts of cold, and 3 parts of boiling water; it is much less soluble in dilute nitric acid, so that the latter generally produces a precipitate in an aqueous solution of this salt; it is for this reason, also, that moderately concentrated nitric acid will not act upon carbonate of baryta. Nitrate of baryta is insoluble in alcohol. This salt is sometimes employed for the detection of acids in analysis, and is the source from which we prepare baryta.

Chlorate of Baryta (BaO.ClO₃) may be prepared by decomposing a hot solution of chlorate of potassa with a slight excess of hydrofluosilicic acid, filtering,

and saturating the solution with carbonate of baryta; the filtered liquid, when evaporated, yields crystals of the chlorate.

Another process consists in decomposing the chlorate of ammonia with carbonate of baryta, and allowing the filtrate to crystallize. For this purpose, 122.6 parts of chlorate of potassa, and 167 parts of bitartrate of ammonia are dissolved in the smallest possible quantity of boiling water, and the bitartrate of potassa allowed to crystallize out. The solution is then mixed with an equal volume of alcohol, to precipitate the remainder of the bitartrate of potassa, filtered, and digested with freshly precipitated carbonate of baryta.

Sulphite of Baryta, BaO.SO_2 , is precipitated in fine needles when sulphite of soda is added to chloride of barium.

SULPHATE OF BARYTA, BaO.SO_4 .

§ 188. We have already mentioned this salt, as found native in the form of *heavy-spar*. It may be prepared very readily by precipitating a hot solution of chloride of barium with dilute sulphuric acid in excess, heating the solution to ebullition, collecting the precipitate on a filter, and washing with hot water till the washings are no longer acid.

Properties.—The crystals of heavy-spar belong to the right prismatic system; their specific gravity is 4.4. The precipitated sulphate of baryta is a white powder.

Sulphate of baryta fuses at a very high temperature to a white enamel; when mixed with carbon and heated to redness, it is reduced to sulphide of barium:—



When boiled with a solution of carbonate of potassa or of soda, or better, if fused with these salts, it is decomposed into carbonate of baryta and sulphate of potassa or soda; if sulphate of baryta be fused with hydrate of potassa, sulphate of potassa is formed, together with hydrate of baryta. It is almost perfectly insoluble in water and dilute acids; it is soluble in concentrated sulphuric acid to some extent, but is reprecipitated by water.¹

When sulphate of baryta is precipitated from a solution containing other salts, especially nitrate of baryta, a portion of the latter is carried down with the sulphate, and can only be separated from it by long washing with hot water. Nitrate of soda may also be carried down in this way, in considerable quantity.

When sulphate of baryta is fused with chloride of calcium, chloride of barium is produced, together with sulphate of lime, whereas, if a solution of the latter salt be added to solution of chloride of barium, the decomposition is reversed, sulphate of baryta and chloride of calcium being formed.

Sulphate of baryta is the source from which all baryta-compounds are usually prepared. It is sometimes used instead of white lead as a pigment, but is more frequently employed to adulterate that substance (see White Lead). This salt also receives application as a flux in copper smelting.

Seleniate of Baryta, BaO.SeO_4 , is precipitated when chloride of barium is added to solution of selenic acid or a seleniate; it resembles the sulphate in its insolubility in water and in dilute acids; when boiled with hydrochloric acid, however, it dissolves, being converted into chloride of barium, with liberation of selenious acid and chlorine:—



The *Phosphate of Baryta* are precipitated by chloride of barium from the

¹ A boiling solution of sulphate of baryta in concentrated sulphuric acid deposits, on cooling, needles of the formula $\text{BaCl}_2 \cdot \text{H}_2\text{SO}_4$, known as *phosphate of baryta*; this salt is decomposed by water into sulphate of baryta and free sulphuric acid.

corresponding soda-salts. They are sparingly soluble in water, but soluble in hydrochloric or nitric acid.

CARBONATE OF BARYTA, $\text{BaO} \cdot \text{CO}_2$.

§ 189. This compound occurs in nature as the mineral *witherite*. When, as is often the case, the pure freshly precipitated carbonate is required, it is prepared by precipitating solution of chloride of barium with a slight excess of carbonate of ammonia, and washing, by decantation, with hot water, till the washings are not rendered turbid by excess of nitric acid and nitrate of silver.

Properties.—*Witherite* is found crystallized in rhombohedra, of spec. grav. 4.3.

The precipitated carbonate of baryta is a soft, white powder; when very strongly heated, it fuses, and loses its carbonic acid at a very high temperature; when very finely divided and suspended in water, it has an alkaline reaction. Carbonate of baryta is poisonous; it is nearly insoluble in water, but dissolves in solution of carbonic acid, and very readily in dilute hydrochloric or nitric acid; it is also slightly soluble in solution of chloride of ammonium in the cold, but if long boiled with this reagent, it dissolves with decomposition:—



the carbonate of ammonia being carried off with the steam.

Carbonate of baryta is decomposed by steam at a bright red heat, hydrate of baryta being formed.

If carbonate of baryta be suspended in a solution of an equal weight of sulphate of potassa or of soda, in the cold, and frequently agitated, sulphate of baryta will be formed, and an alkaline carbonate found in solution, but if the mixture be boiled, the decomposition will be reversed.

Native carbonate of baryta is used for the preparation of other salts of baryta; the freshly precipitated carbonate is sometimes employed in the preparation of organic substances, for removing free sulphuric acid, or for decomposing the soluble sulphates of organic bases.

Carbonate of baryta is dissolved by a solution of carbonic acid, *bicarbonate of baryta* being produced, which has not been obtained in a solid state.

Sesquicarbonate of Baryta, $2\text{BaO} \cdot 3\text{CO}_2$, is precipitated when chloride of barium is decomposed by sesquicarbonate of soda.

A *Borate* and a *Biborate of Baryta* may be precipitated by adding chloride of barium to the corresponding salts of soda. They are sparingly soluble in water, but easily in hydrochloric or nitric acid.

BINOXIDE OF BARIUM, BaO_2 .

§ 190. This substance is precipitated in the form of a crystalline hydrate, when an excess of baryta-water is added to binoxide of hydrogen.

Preparation.—Fragments of anhydrous baryta are heated to low redness in a green glass retort, and a current of dry oxygen passed over them; the appearance of the fragments is scarcely altered.

The binoxide may also be prepared by gradually adding about 1 part of ohlorate of potassa to 4 parts of baryta, heated to low redness in a porcelain crucible. The mass, which contains binoxide of barium and chloride of potassium, is washed with cold water, when the binoxide is left as a hydrate.

Properties.—Binoxide of barium combines with water, without evolution of heat, to form a hydrate ($\text{BaO}_2 \cdot 6\text{HO}$), which is a white, very slightly soluble powder; when this is boiled with water, oxygen escapes, and baryta is found in solution.¹

¹ Binoxide of barium also loses half its oxygen, when heated alone to a very high temperature; but, in an atmosphere of steam, this decomposition may be effected, as Boussingault has recently shown, at a much lower temperature.

It is very easily decomposed by deoxidizing agents; when heated in hydrogen, it yields hydrate of baryta, and gives up its second equivalent of oxygen to carbon, phosphorus, sulphur, boron, and the metals at elevated temperatures; when dissolved in hydrated acids, a salt of baryta is formed, together with bin-oxide of hydrogen:—



this decomposition is taken advantage of for the preparation of the latter compound.

Bin-oxide of barium is also used in the preparation of certain of the rarer metallic peroxides, and has lately been proposed as an oxidizing agent in analysis.

It has also been recently employed by Boussingault for the extraction of oxygen from atmospheric air (§ 69).

CHLORIDE OF BARIUM, MURIATE OF BARYTES, BaCl.

§ 191. This salt is formed when chlorine is passed over baryta at a high temperature, oxygen being expelled.

Preparation.—Native carbonate of baryta may be dissolved in dilute hydrochloric acid, to saturation, and the solution evaporated to the crystallizing point. Another method consists in decomposing solution of sulphide of barium with a slight excess of hydrochloric acid, boiling, filtering to separate a little precipitated sulphur, and crystallizing.

On the large scale, chloride of barium is prepared by calcining a mixture of powdered heavy-spar (sulphate of baryta) with half its weight of chloride of calcium (the residue from the preparation of ammonia) in a reverberatory furnace; the mass is exhausted, as rapidly as possible, with hot water, which leaves the sulphate of lime undissolved, and the clear solution of chloride of barium decanted and evaporated.¹

The salt prepared by any of the above processes should be purified by recrystallization.

Properties.—Chloride of barium forms colorless tabular crystals, of the formula $\text{BaCl} + 2\text{Aq}$; these are unaltered in air; when heated, they decrepitate, and lose their water; the anhydrous salt thus obtained fuses at a red heat, and when strongly heated, in the presence of aqueous vapor, it is partly converted into baryta. The fused salt absorbs 2 eqs. of water from the air. 1 part of the crystals dissolves in about 2.3 parts of cold and 1.3 of boiling water. This chloride is much less soluble in dilute hydrochloric acid, so that an addition of this acid causes a precipitate in the aqueous solution. Chloride of barium is almost insoluble in absolute alcohol.

This salt is constantly used as a reagent for the detection of various acids.

Wurtz has also recently employed it in the analysis of certain siliceous minerals, since he found that many insoluble silicates, when fused with anhydrous chloride of barium, were converted into masses which were decomposed by hydrochloric acid.

Fluoride of Barium (BaF) is precipitated when chloride of barium is added to solution of fluoride of potassium.

SULPHIDE OF BARIUM, SULPHURET OF BARIUM, BaS.

§ 192. Sulphide of barium is formed when hydrosulphuric acid acts on baryta, or when hydrogen is passed over sulphate of baryta at a red heat.

Preparation.—It is best prepared by mixing powdered heavy-spar with about $\frac{1}{2}$ of its weight of charcoal, and enough oil to form a paste; this is thoroughly

¹ Another method consists in fusing heavy-spar with chloride of calcium, iron-filings, and charcoal, when chloride of barium, sulphide of iron, and (insoluble) oxysulphide of calcium are produced; the mass is then treated with boiling water.

incorporated, and maintained at a red heat, in an earthen crucible, till no more carbonic oxide escapes:—



The sulphate of baryta is sometimes mixed with $\frac{1}{2}$ lampblack, $\frac{1}{2}$ resin, and $\frac{1}{2}$ starch, made up into balls with a little water, and these carbonized in a coal fire.¹

The black mass is powdered, boiled with a small quantity of water, and filtered while hot; on cooling, the sulphide of barium crystallizes out in thin, nearly colorless plates. If the sulphide be required for the preparation of some other salt of barium, the crude mass obtained as above may be boiled with a larger quantity of water, so that the solution shall not crystallize on cooling.²

Properties.—The crystals appear to contain 6 eqs. of water. When exposed to the air, sulphide of barium is decomposed by the atmospheric water and carbonic acid, evolving sulphuretted hydrogen:—



Sulphide of barium is oxidized by steam, at a red heat, hydrogen being evolved, and sulphate of baryta produced.

When sulphide of barium is dissolved in water, it appears to undergo partial decomposition,³ hydrate of baryta and hydrosulphate of sulphide of barium being formed; double compounds of baryta with sulphide of barium (crystallizing with water) are also produced under these circumstances.

The aqueous solution of sulphide of barium, when exposed to the air, absorbs oxygen, first becoming yellow from the production of a higher sulphide, and afterwards depositing crystals of *hyposulphite of baryta* ($\text{BaO.S}_2\text{O}_3$).

Sulphide of barium is a sulphur-base. *Hydrosulphate of sulphide of barium* (BaS.HS) may be prepared like the corresponding compound of potassium.

Barium forms also a *tersulphide* (BaS_3), and a *pentasulphide* (BaS_5).

Silicofluoride of Barium, $3\text{BaF}.2\text{SiF}_2$, is thrown down as a crystalline precipitate, when hydrofluosilicic acid is added to chloride of barium; this compound is very sparingly soluble in water and acids, and is decomposed by heat into fluoride of barium and terfluoride of silicon, which escapes.

STRONTIUM.

Sym. Sr. Eq. 43.8.

§ 193. This metal was first obtained by Sir H. Davy, in 1808. It is named from Strontian, in Argyleshire, where it was first discovered.

Strontium is by no means so abundant in nature as barium; it occurs chiefly in the forms of sulphate and carbonate, and is found in small quantity in certain mineral waters. It may be prepared by the same methods as barium, which it

¹ When sulphate of baryta, free from iron, is ignited with a small quantity of carbonaceous matter, a mass possessed of phosphorescent properties is obtained, which is termed *Bologna phosphorus*.

² When the sulphide of barium is prepared below a bright red heat, the aqueous solution obtained from the ignited mass contains much hydrate of baryta and a higher sulphide of barium.

³ When the mass obtained in the preparation of sulphide of barium is treated with successive small portions of water, the first two solutions are yellow, and contain considerable quantities of hydrosulphate of sulphide of barium and the higher sulphides of barium; the third is a solution of nearly pure sulphide of barium, while the succeeding solutions contain gradually increasing quantities of baryta, the last being nearly pure baryta-water.

much resembles in its appearance, properties, and combinations. It is heavier than oil of vitriol, and less fusible than barium.

STRONTIUM AND OXYGEN.

Strontia	SrO
Binoxide of Strontium	SrO ₂

OXIDE OF STRONTIUM, STRONTIA.

SrO. Eq. 51.8.

The oxide of strontium is prepared from the native carbonate or sulphate, in exactly the same way as baryta. It is similar to that oxide in its properties, and combines with water very energetically, to form hydrate of strontia.

Crystallized hydrate of strontia has the formula SrO.HO + 9Aq, and is easily converted into carbonate by exposure to air. At 212° F. (100° C.) it loses the whole of its water of crystallization, becoming converted into SrO.HO, which is not decomposed at a red heat.

NITRATE OF STRONTIA, SrO.NO₃.

This salt is prepared in the same manner as nitrate of baryta.

The ordinary crystals are anhydrous, colorless octohedra, which decrepitate when heated, and are ultimately decomposed, leaving anhydrous strontia. They are soluble in five parts of cold, and in considerably less of boiling water, and insoluble in absolute alcohol. At a low temperature, the solution deposits prismatic crystals, of the formula SrO.NO₃ + Aq, which effloresce in air.

Nitrate of strontia is employed in the preparation of the *red fires* used upon the stage, and in fireworks; a common mixture for these purposes consists of 40 parts of nitrate or strontia, 13 of flowers of sulphur, 10 of chlorate of potassa, and 4 of tersulphide of antimony.

SULPHATE OF STRONTIA (SrO.SO₄) is found in nature in the form of *celestine*, crystallized in rhomboidal prisms, and in considerable quantity, associated with sulphur, in the neighborhood of volcanoes; it is the commonest mineral of strontia.

The sulphate may be prepared artificially by precipitating a solution of nitrate of strontia with sulphuric acid. Its properties exactly resemble those of sulphate of baryta; it is somewhat more soluble in water and acids. It may be completely dissolved by a solution of common salt.

Carbonate of strontia (SrO.CO₃) constitutes the mineral known as *strontionite*;¹ its crystals belong to the right prismatic system; it may be prepared in the same manner as carbonate of baryta. Its properties resemble those of the latter, but its carbonic acid is more easily expelled.

The *Binoxide of Strontium* (SrO₂) is deposited as a hydrate, in crystalline scales, when a solution of binoxide of hydrogen is added to a solution of strontia. This substance cannot be formed, like the binoxide of barium, by passing oxygen over heated baryta.

Chloride of Strontium (SrCl) is obtained by decomposing the carbonate or sulphide with hydrochloric acid; it forms deliquescent needles of the formula SrCl + 6Aq, which lose all their water when gently ignited; they are very soluble in water, and moderately so in alcohol. This salt is almost insoluble in concentrated hydrochloric acid.

The *Sulphide of Strontium* exactly resemble those of barium in preparation and properties.

¹ Carbonate of strontia is also found in some mineral waters.

CALCIUM.

Sym. Ca. Eq. 20.

§ 194. We are indebted for the discovery of calcium to Sir H. Davy, who first obtained it, in 1808.

The natural sources of this metal are very numerous; it occurs chiefly in the forms of carbonate of lime, which constitute the different varieties of limestone, chalk, and marble, found in all parts of the world. Gypsum, the sulphate of lime, is another form in which this metal occurs. Phosphate of lime is also found in the mineral kingdom. Fluoride of calcium constitutes the mineral known as fluor-spar.

This metal is obtained in the same way as barium, and is very similar to it. It combines with oxygen to form an oxide, CaO , and a binoxide, CaO_2 .

CALCIUM AND OXYGEN.

Lime	CaO
Bin oxide of calcium	CaO_2

OXIDE OF CALCIUM, LIME, QUICKLIME.

CaO. Eq. 28.

Preparation.—This very useful substance is prepared by the decomposition of carbonate of lime by heat. The operation is carried out on a very large scale in kilns or furnaces, so constructed that the products of combustion of the fuel (wood, turf, or, sometimes, coal), shall pass through the carbonate; for it is found that the carbonic acid is much more easily expelled when the carbonate is heated in a stream of another gas, than in a crucible.

The various forms of carbonate of lime do not give up their carbonic acid with the same facility, in consequence of the difference in their texture; chalk or limestone is much more easily decomposed than marble, and, being much more abundant, is always employed on the large scale. Moist limestone is much more easily caustified than that which is perfectly dry.

The *lime-kilns* are of two kinds, in one of which the process is interrupted after every operation, whilst in the other it is continuous.

The simplest form of lime-kiln is a tall conical furnace, over the hearth of which the lime-burner constructs an arch with large lumps of the limestone to be burnt; upon this arch the rest of the limestone is heaped, so as to fill up the furnace; the fire is then kindled, and the operation allowed to continue (for about three days and nights), until the whole of the lime is thoroughly burnt. The heat is raised gradually, so that the stones forming the arch may not crack.

The continuous lime-kiln is an inverted cone of brick-work, with an aperture at the lower part, through which the burnt lime is withdrawn. A layer of brushwood is placed at the bottom, upon this a layer of coal, then a layer of limestone, the coal and limestone being arranged in alternate layers, until the kiln is filled. The fire is then lighted, and as soon as the upper layers have sunk in the mouth of the kiln, fresh charges of coal and limestone are introduced. The lime is raked out from the bottom at intervals of about half an hour.

The lime thus obtained is by no means pure; it usually contains silica, alumina, and sesquioxide of iron, derived from the limestone, together with alkaline sulphates and chlorides from the ashes of the fuel. For many purposes the

presence of the three former impurities is of no consequence, and the lime may be freed from the two latter by slaking it, throwing the hydrate upon a filter, washing with water till the washings are no longer rendered turbid by nitrate of silver (after acidulating with nitric acid), and igniting the purified hydrate in an earthen crucible.

Very nearly pure lime may also be obtained by heating oyster-shells, or fragments of Carrara marble, to bright redness, either in an open fire, or in an earthen crucible with a hole in the bottom.

Lime of absolute purity may be prepared by saturating dilute nitric acid with powdered marble, evaporating to dryness, and igniting the residual nitrate.

Properties of Lime.—Anhydrous lime, or quicklime, is a soft, white, amorphous solid, of specific gravity varying between 2.5 and 3. It preserves the external appearance which the carbonate presented before ignition. Ordinary quicklime has usually a gray color, probably due to a trace of carbon. Lime is one of the most infusible bodies which we possess; it resists the highest heat of our furnaces. A mass of lime heated in the flame of the oxyhydrogen blow-pipe emits a most dazzling white light, and fuses at the edges.

When exposed to air, quicklime very soon absorbs water, the lumps crumbling to a bulky powder, which is *hydrate of lime*, or *slaked lime*; when a mass of lime is moistened with water, very energetic combination takes place, and occasionally a slight explosion, due to the sudden evolution of steam; the mass splits in all directions, and finally crumbles to a dry powder of hydrate; the slaking takes place more rapidly, and a more finely-divided hydrate is obtained when hot water is employed.* Ordinary quicklime frequently contains fragments which will not slake, but are left as cinder-like masses in the midst of the hydrate; these masses appear to consist of semi-fused silicate of lime, and are most frequently found in lime which has been *over-burnt*, i. e. calcined at too high a temperature.†

Besides silicic acid, quicklime often contains magnesia, alumina, &c. When it contains large quantities of these impurities it slakes very feebly, and is called *poor lime*, but if it be pretty pure and slakes easily, it is termed *fat lime*.

Uses.—Quicklime is used chiefly for the preparation of mortar, and for agricultural purposes. It is very useful in the laboratory for drying certain gases, for abstracting the water from alcohol, and for decomposing various organic substances.

HYDRATE OF LIME. SLAKED LIME, CaO.HO .

The hydrate is always prepared by slaking quicklime.

Preparation.—It forms a fine white powder, which loses its water at a red heat, but does not fuse. When exposed to air, it absorbs carbonic acid, and is converted into a mixture of carbonate of lime and hydrate of lime; after long exposure it ceases to absorb carbonic acid, and is then found to contain single equivalents of hydrate and carbonate.

Hydrate of lime is very sparingly soluble in water, 1 part requiring about 1400 parts of water; it is less soluble in hot water than in cold, so that a cold saturated solution becomes turbid when heated to the boiling point.‡ *Lime-water* should therefore always be prepared with cold water: the best plan is to place a considerable quantity of fresh slaked lime, previously washed with water to remove soluble salts, in a large bottle, which is then filled up with cold distilled

water. The solution is the more finely filtered when a large quantity of water has been used than the more concentrated solutions.

When a small quantity of the slaked lime has been immersed in water, forms a heavy mass which, on comparison, is found to be composed of hydrate and carbonate of lime.

When a large quantity of the slaked lime is immersed in water, the water is not re-absorbed to any perceptible extent when the water is not over-boiled.

water, and shaken from time to time; it is then allowed to stand, in order that the excess of lime may subside; the bottle should always be kept filled with water. If a saturated solution of hydrate of lime be evaporated *in vacuo* over oil of vitriol, it deposits the crystallized hydrate in six-sided tables.

Lime-water has a distinct alkaline reaction, and a feebly alkaline taste. When lime-water is exposed to air, a pellicle of carbonate forms upon its surface, and if this be broken, a fresh pellicle forms until all the lime is precipitated; hence, lime-water must be kept in well-closed bottles.

A mixture of finely divided hydrate of lime with water, is termed *milk* or *cream of lime*, according to its consistence. Hydrate of lime is much more soluble in solution of sugar than in pure water; the solution is usually known as *sugar-lime*, and is useful in the laboratory.

§ 195. USES OF HYDRATE OF LIME.—This substance is applied to numerous purposes in the arts and manufactures. It is chiefly employed in the preparation of *mortar* for building purposes; this is usually composed of 1 part of freshly-slaked lime, and 2 or 3 parts (or even more, according to the quality of the lime) of sand, mixed with water to a paste, which is spread in a thin layer between the stones to be cemented.

The *hardening of mortar* is explained partly on mechanical, partly on chemical principles. The chief chemical alteration which mortar undergoes, consists in the conversion of a part of the lime into carbonate, which is capable of combining with unaltered hydrate of lime, to form a solid mass. It also appears that the deposition of minute crystals of carbonate of lime helps materially to bind the particles together. These reasons may afford a satisfactory explanation of the rapid *setting* of the mortar; but direct experiments and analyses of very old mortars have shown that its ultimate conversion into a hard stone-like mass, must be attributed in great measure to the formation of a silicate of lime, by the action of lime upon the sand, in the presence of moisture. The sand has, moreover, a most important mechanical effect in preventing the mass from shrinking too much when dried, and in forming a number of *nuclei* around which the lime adheres.

The nature of the sand is not without influence upon the quality of the mortar; rough irregular grains are preferable to those which are quite smooth; the sand should also be as pure as possible. Mortar does not set firmly when dried too quickly; hence it sets better in temperate seasons than in hot summers.

Water containing much alkaline chloride should not be employed for the preparation of mortar, since its action upon lime would give rise to the production of chloride of calcium, which would prevent the drying of the mortar.

Hydraulic mortars and cements are such as set under water, and are not disintegrated by its action. These are usually prepared either from natural or artificial mixtures of carbonate of lime with silica, or silicate of alumina or of magnesia.

They are prepared from limestones containing certain proportions of the three latter ingredients. When a limestone of this description is calcined, a double silicate of alumina (or magnesia) and lime is formed, which is capable of combining with water to produce a compact hydrate which resists the action of that solvent.

Even *dolomite* (carbonate of lime and magnesia) calcined at a moderate heat, exhibits the property of a hydraulic lime; and half-burnt lime (containing still a certain quantity of carbonate) will also set under water.

In order that a limestone containing silica may be employed for the production of hydraulic lime, it is necessary that this ingredient be present in a state in which it is capable of entering readily into combination with the lime, which is the case with the silica contained in clay. If carbonate of lime be mixed with gelatinous silica, a good cement is obtained on calcination, but if sand or rock-

crystal be employed, the resulting product is valueless. These clays are best fitted for the production of cements which yield a portion of their silica to a solution of potassa.

If an hydraulic lime be calcined at too high a temperature, the silicates undergo a partial fusion, and will not set afterwards under water. The heat employed should be only just high enough to expel the water from the clay, and the greater part of the carbonic acid from the carbonate of lime.

Neither clay (silicate of alumina) nor lime, alone, will set under water, but if an intimate mixture of clay and chalk be calcined at a moderate heat, and afterwards mixed with water, a hydrated double silicate of alumina and lime is formed as a hard mass, which yields gelatinous silica when treated with acids, although no silica can be separated in this manner from ordinary clay. If the clay or limestone should contain a little alkali, it appears to promote the solidification of the cement by carrying the silica to the lime.

When clay which has been dried at a moderately high temperature is immersed in lime-water, it slowly extracts the lime, depriving the solution of its alkaline reaction. Hydrated alumina and gelatinous silica act in a similar manner, but more slowly. Hence it appears that clay, and, to some extent also, alumina and silica, are capable of forming insoluble compounds with lime, even at ordinary temperatures.

One variety of hydraulic lime is simply a poor lime, containing 10 or 15 per cent. of clay; when such lime is slaked and made into a paste with water, it is found to set, even under water, after some time, in consequence of a combination between the silicate of alumina (clay) and the lime. Cements similar to this, prepared by the judicious calcination of certain argillaceous limestones, are known as *Roman cement*, *Portland cement*, &c.; they contain from 10 to 35 per cent. of clay; those which contain most of this ingredient solidify most rapidly. Limestones containing 8 to 12 per cent. of clay furnish a hydraulic lime, which hardens under water in 15 or 20 days. When they contain 15 to 18 per cent. of clay, the hardening takes place in 8 days. If the clay amount to 25 per cent. the resulting cement will set in 3 or 4 days.

Roman cement contains about 35 per cent. of clay, and hardens even within an hour, if of good quality.

The amount of clay contained in any specimen of limestone may be readily determined by treating it with dilute hydrochloric acid, when the clay is left undissolved, and may be collected on a filter, well washed, dried, ignited, and weighed.

The Roman cement was originally made by calcining a mixture of slaked lime and *puzzolano*¹ (a rock of volcanic origin found near Naples), but is now prepared from masses of argillaceous limestone (containing 30 per cent. of clay) procured from the bed of the Thames, and other parts of the London clay. Limestones which contain more than 35 per cent. of clay do not furnish a cement when burnt. Hydraulic limes are sometimes made artificially, by mixing lime and clay in proper proportions.²

Hydraulic mortar of good quality may be known by its not showing any tend-

¹ This mineral is remarkable for the readiness with which it combines with lime, being capable even of extracting it from its solution in water. Most of the tufas of volcanic origin present the properties of puzzolano, and are found in various localities: puzzolano may also be replaced by many varieties of common clay calcined at a moderate heat.

A variety of puzzolano, not of volcanic origin, has lately been discovered by Sauvage in the Dep. des Ardennes. It contains 50 per cent. of soluble silica: see § 1371.

² An excellent cement is made in the neighbourhood of Paris, and used for many public works in that city, from 1 part of clay and 4 parts of chalk: these are intimately mixed with water, afterwards allowed to settle, and the deposit thus obtained is moulded into bricks, which are fired and calcined at a gentle heat. This hydraulic lime, like the best obtained from natural sources, is entirely dissolved by acids.

ency to crack when hardened under water, by its acquiring a very considerable degree of hardness in a short time, and afterwards resisting the action of water. The surfaces of the stones should always be moistened before the mortar is applied. A certain quantity of sand is always added to hydraulic mortar, to prevent excessive shrinking.

Hydraulic lime will not harden if it be immediately placed in water, without having acquired a certain consistence. Care should be taken to prevent it from attracting moisture to any extent from the atmosphere, as its quality is then much deteriorated.

The solidification of hydraulic lime is much promoted by a high temperature and increased pressure.

Ransome's vitrified cement is prepared by boiling flints, under pressure, with caustic soda or potassa, when a solution of alkaline silicate is obtained, which is intimately mixed with 1 part of pipe-clay, 1 part of powdered flint, and 10 parts of sand; the mixture is pressed into moulds, dried, and carefully annealed.

Alum-shale, ashes of coal, &c., are sometimes used instead of clay for the manufacture of cement.

The hydraulic mortar of Tournay is prepared from the refuse of the lime-kilns (containing lime and coal-ashes in the proportion of about 1 : 3), which is slaked with water and well mixed.

Certain iron and copper slags have also been found to afford excellent cements when mixed with burnt lime.

In order to ascertain whether a slag is fitted for this purpose, it is digested, in the state of fine powder, with a little hydrochloric acid; if much gelatinous silica be separated, the slag may be used for preparing a cement.

Lime is also employed as a manure; its action in this capacity can scarcely be said to be thoroughly understood, but it appears to depend, to a slight extent, upon its furnishing an adequate supply of lime for the crops, and in a much greater degree, upon its promoting the decay of the organic matters contained in the soil, hastening their conversion into carbonic acid and ammonia, from which the plants appear to derive their food. The lime may also be useful in decomposing minerals containing potassa, and converting this base into a soluble form. In some cases, lime containing magnesia has been found injurious to plants.

Large quantities of hydrate of lime are employed in the preparation of ammonia and of bleaching-powder, and in the purification of gas; it is also extensively employed by the candle-maker, the soap-boiler, the cotton-printer, the tanner, and the sugar-refiner. In medicine, lime-water is used as an *antacid*.

The chemist devotes hydrate of lime to a variety of uses; it serves him to prepare the caustic alkalies, and to absorb carbonic acid; it is also used as a reagent.

Nearly all those salts of lime which are neutral in constitution are neutral to test-papers.

NITRATE OF LIME, $\text{CaO}\cdot\text{NO}_2$,

§ 196. This salt sometimes effloresces on the walls of cloacæ, &c., being formed by nitrification (*see* § 144). It is also produced in the nitre-beds by the same process.

Nitrate of lime is prepared by saturating dilute nitric acid with carbonate of lime, and evaporating to crystallization. It crystallizes in six-sided prisms, of the formula $\text{CaO}\cdot\text{NO}_2 + 4\text{Aq}$; they are very deliquescent, and soluble in water; concentrated nitric acid, added to the aqueous solution, produces a crystalline precipitate of the nitrate. When heated, the crystals fuse, lose their water easily, and are finally decomposed into lime, peroxide of nitrogen, and oxygen. Nitrate of lime sometimes finds an application in consequence of its great

attraction for water; this salt is also an intermediate product of the nitre manufacture.

Nitrate of lime is capable of combining with lime to form two basic salts.

HYPOCHLORITE OF LIME, $\text{CaO} \cdot \text{ClO}$.

§ 197. This salt is prepared by adding solution of hypochlorous acid to milk of lime, so that the latter may remain in excess; it is only known in solution, which bleaches test-papers, and is easily decomposed into chlorate of lime and chloride of calcium. In mixture (or combination?) with 1 equivalent of chloride of calcium, it forms the well known *chloride of lime*.

HYPOCHLOBITE OF LIME WITH CHLORIDE OF CALCIUM. CHLORIDE OF LIME. BLEACH. $\text{CaO} \cdot \text{ClO} + \text{CaCl}$.

This compound, which is so important in the arts, is obtained by the action of chlorine upon an excess of hydrate of lime.

If an *excess of chlorine* be brought in contact with hydrate of lime, chloride of calcium and chlorate of lime are formed:—



but if the *hydrate of lime* be in *excess*, the decomposition is as follows:—



This process is carried out on a very large scale; the chlorine is slowly generated, in a leaden or stone retort heated by steam, from a mixture of binoxide of manganese, chloride of sodium, and oil of vitriol, or from binoxide of manganese and the hydrochloric acid obtained from the alkali-works (with which the bleach-factory is often in connection), and is passed into chambers of brickwork, in which hydrate of lime is spread out upon trays placed one above the other.¹ In this process, the temperature should not rise above 62° F. (16°.5 C.), or much chlorate of lime will be produced. When the chloride of lime is to be used in solution, it is often made on the spot by passing chlorine into an excess of milk of lime kept in continual agitation.

Properties.—The substance termed chloride of lime is a white, somewhat moist powder, the formula of which, if pure, would be $\text{CaO} \cdot \text{ClO} + \text{CaCl} + 2\text{Aq}$; it contains, however, besides these, an excess of hydrate of lime, and a certain amount of carbonate. When exposed to air, it continually evolves hypochlorous acid, in consequence of the action of the carbonic acid upon the hypochlorite of lime: it also deliquesces rapidly. When heated, it loses water, and is converted into a mixture of chloride of calcium and chlorate of lime:—



the chlorate of lime is afterwards decomposed by the heat, with evolution of oxygen. When chloride of lime is shaken with about 10 parts of cold water, the chloride of calcium and hypochlorite of lime are dissolved out together with a little hydrate of lime, leaving the remainder of the hydrate, and the carbonate of lime. The solution has an alkaline reaction to test-papers, which it afterwards bleaches, by reason of its oxidizing action upon the coloring matter; if the solution be boiled, it loses its bleaching properties and is found to contain chlorate of lime and chloride of calcium.

When exposed to air, solution of chloride of lime evolves hypochlorous acid,

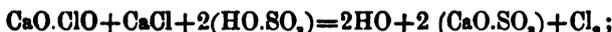
¹ The chlorine is usually passed through a little water, to remove hydrochloric acid, &c., and afterwards over soda-lime, which it is of course to continually trickling, to remove the water.

and deposits carbonate of lime. When the solid chloride of lime, or its solution, is kept for any length of time, it decomposes according to the equation :—



so that it is advantageous to use it freshly prepared.

If chloride of lime be treated with an excess of acid, even of carbonic acid, it evolves chlorine :—



and, by means of the nascent chlorine, a mixture of chloride of lime and free acid bleaches much more powerfully than the chloride alone. If the acid be added in small quantity, hypochlorous acid is evolved.

Uses of Chloride of Lime.—This substance is the chief bleaching agent employed for cotton and linen; it is generally used in conjunction with an acid. The stuff is first *soured*, as it is termed, in a bath of very dilute (sulphuric) acid, then steeped in the bath of chloride of lime, afterwards soured again, and finally washed in an alkaline lye.

The superior bleaching power of a mixture of chloride of lime with an acid is taken advantage of in cotton printing, for the production of white patterns upon a colored ground. The pattern is printed upon a madder-red ground, for example, with solution of tartaric acid thickened with gum; it is then immersed for a very short time in the bleaching liquor, when the color is discharged in those parts only which were impregnated with the acid.

Chloride of lime is also employed to destroy the gaseous poisons with which the atmosphere of sick-rooms, and other localities, is contaminated; the hypochlorous acid evolved from the compound by the action of the carbonic acid of the air, oxidizes and destroys the *miasmata*; in this application, the solution of chloride of lime is sometimes sprinkled over the floor of the room; sometimes a cloth is saturated with it, and hung up in the air, or, in extreme cases, as where large quantities of sulphuretted hydrogen, emanating from cloacæ, &c., are to be destroyed, the powder itself is mixed with dilute sulphuric acid, added by small portions at a time, in a shallow vessel. A mixture of bleaching powder and alum is particularly well suited for this purpose.

Chloride of lime is occasionally used in the laboratory as an oxidizing agent.

When we remember the circumstances which may alter the composition of chloride of lime—viz: the extent to which the lime was saturated with chlorine, the degree of humidity of the lime, and the length of time for which the bleach, when prepared, has been kept in store, as well as the nature of the place in which it has been kept, we shall not wonder that various samples of bleaching powder contain very different quantities of available chlorine.

Good, freshly prepared bleach contains 30 per cent. of available chlorine, but specimens are sometimes met with which contain only 10 per cent.

Several methods are in use for the determination of the value of specimens of bleach, which operation is usually termed *chlorimetry* (see Quantitative Analysis, Special Methods).

SULPHITE OF LIME, $\text{CaO}.\text{SO}_2 + 2\text{Aq}$.

§ 198. This salt may be prepared in a similar manner to sulphite of soda, substituting the hydrate, or carbonate of lime, in a fine state of division, for the solution of soda.

Sulphite of lime is very sparingly soluble in water; when exposed to air, it becomes covered with an incrustation of sulphate. When heated, sulphite of lime is decomposed into sulphate of lime and sulphide of calcium :—



The sulphite of lime dissolves in solution of sulphurous acid, forming, proba-

bly, an *acid sulphite*. The sulphite may be obtained from this solution in hexagonal needles. Sulphite of lime has been recently employed in the extraction of sugar from beet-root; it has been found that the addition of this substance to the pulp prevents the change of color by exposure to the air, and the loss of sugar by fermentation. This use of sulphite of lime is explained by its proneness to absorb the oxygen of the air.

SULPHATE OF LIME, CaO.SO_4 .

Sulphate of lime is found abundantly in nature. The names, *anhydrite* and *karantite*, are applied to native forms of anhydrous sulphate of lime.

HYDRATED SULPHATE OF LIME, $\text{CaO.SO}_4.\text{HO.} + \text{Aq.}$ occurs as *gypsum*, *alabaster*, and *selenite*. Sulphate of lime is also found in most river and well waters.

It is thrown down as a white precipitate when sulphuric acid is added to a moderately concentrated solution of a salt of lime.

Properties.—*Anhydrite* is a hard, crystalline, compact mineral, of sp. gr. 2.9. It fuses at a red heat, and assumes a crystalline structure on cooling. It cannot be decomposed by heat.

Gypsum is usually found in large masses, compact, micaceous, or fibrous, and occasionally in rhomboidal prisms, which are aggregated together in the form of a spear-head. This mineral is not very hard; it may be scratched even with the nail; its sp. gr. is 2.3.

When heated, hydrated sulphate of lime (gypsum) loses its water at about 258° or 270° F. (121° or 132° C.),¹ and is converted into anhydrous sulphate; this change is effected more easily in a current of air. The mineral then becomes more friable, and if powdered and mixed with water into a paste, this will solidify in a short time, in consequence of the combination of the water with the particles of sulphate of lime. A slight elevation of temperature results from this combination, which is also accompanied by an increase of volume.² If the gypsum be too strongly heated after the water is expelled, it undergoes a partial fusion, and loses this property of recombining easily with water. The dehydrated gypsum gradually absorbs water from the air.

Sulphate of lime is sparingly soluble in water, and is said to present an anomaly similar to that exhibited by sulphate of soda, being most soluble in water at 95° F. (35° C.) Thus:—

100 parts of water at	dissolve of sulphate of lime
32° F. (0° C.)	0.205 part.
68° F. (20° C.)	0.241 “
95° F. (35° C.)	0.254 “
212° F. (100° C.)	0.217 “

The solution is perfectly neutral, and nearly tasteless; when slowly evaporated, it deposits small crystals of the same form as those of native gypsum.

When waters, containing much sulphate of lime, are evaporated in high-pressure boilers, at a temperature of about 248° F. (120° C.) crystals are deposited of the formula $2(\text{CaO.SO}_4) + \text{Aq.}$ The same salt is obtained when native gypsum is heated to about 225° F. (107° C.)

Sulphate of lime is insoluble in alcohol, whence this latter precipitates the salt from its aqueous solution. It dissolves in concentrated sulphuric acid, form-

¹ The water of crystallisation may be expelled at the boiling point, in vacuo, over sulphuric acid.

According to Milton, gypsum becomes anhydrous only at a temperature of from 352° to 372° F. (180° — 200° C.)

² Unburnt gypsum softens also when mixed in powder, with solutions of various salts of potassa, yielding a mass quite similar to common hardened gypsum.

ing, it is said, a *bisulphate*, which is decomposed by water into the neutral salt and hydrated sulphuric acid.

The sulphate is soluble to a considerable extent in hydrochloric acid, and may be afterwards deposited again in crystals. Dilute nitric acid is also capable of dissolving this salt.

Sulphate of lime in a state of solution, allowed to remain in contact with organic matters, is reduced to sulphide of calcium, which, under the influence of water and carbonic acid, is converted into carbonate of lime, with evolution of sulphuretted hydrogen (*page 162*):—



This decomposition frequently takes place in mineral waters which have been kept for some time in contact with cork, and may help to explain the formation of sulphurous waters.

Sulphate of lime is easily reduced to sulphide of calcium by roasting with de-oxidizing agents, *e. g.* carbon. If the sulphide thus obtained be moistened and exposed to a current of carbonic acid, it yields a large supply of sulphuretted hydrogen. Pelouze has proposed to take advantage of this method in the preparation of oil of vitriol, in the event of a rise of price in Sicilian sulphur. If sulphate of lime be mixed with sand, and exposed to a bright red heat (especially if a current of steam be passed over it), silicate of lime is formed, and sulphurous acid passes off, together with oxygen:—



Fremy suggests this as a method of preparing sulphuric acid from gypsum.

Uses of Sulphate of Lime.—Sulphate of lime is used chiefly for taking moulds from objects of which copies are required; in this application advantage is taken of the above-mentioned property which dried gypsum possesses, of setting into a solid mass when mixed with water. In order to prepare the gypsum for this use, the masses of the mineral are heated in kilns (sometimes built up with the masses themselves) to a temperature below 392° F. (200° C.), until all the water is expelled; they are then ground in a mill, and sent into commerce under the name of *plaster of Paris*. The quality of the plaster thus obtained depends in great measure upon the temperature employed, since, as before stated, the burnt gypsum combines very slowly with water, if it has been exposed to too high a temperature.¹

It has been proposed, of late years, to employ steam at a high pressure for this purpose (the gypsum being placed in ovens heated externally by steam), and the process is said to be successful. Some specimens of plaster of Paris evolve sulphuretted hydrogen when mixed with water; this is due to the presence of sulphide of calcium produced by the reduction of the sulphate, by the action of the flame in the kiln; very fine plaster is burnt out of contact with the flame. Plaster of Paris becomes useless after long exposure to the air, since it is gradually converted into the hydrated sulphate. The best plaster is that found in the neighborhood of Paris, the superiority being probably due to the presence of a small quantity of carbonate of lime and of clay.

The quality of any specimen is best ascertained by actual trial, but the temperature observed during the setting of the plaster is a good indication.²

The slight expansion in the setting of the plaster renders it particularly appropriate for taking moulds, since it forces the material into every line of the model. Plaster of Paris is also largely used as a cement for building purposes.

¹ Experience has shown that gypsum, entirely deprived of its water, does not harden so rapidly as that which has only been heated, until the tumultuous expulsion of vapor has ceased, when the gypsum still retains one-fourth its water.

² Gay-Lussac has observed that the hardness of plaster casts is to some extent proportional to that of the original unburnt gypsum.

Stucco consists of plaster which has been mixed with water containing gelatin (size) or gum in solution; it is capable of receiving a high polish, and may be variously colored.

A composition containing plaster of Paris and alum has been lately introduced for taking casts, and is not only harder than ordinary plaster, but possesses somewhat the appearance of marble, and is capable of resisting the action of moisture in a higher degree than common plaster. In order to prepare this material, the gypsum, having been burnt in the ordinary manner, is soaked in a saturated solution of alum for some hours, and then again burnt at a dull red heat. This plaster takes longer to set than the ordinary kind. When mixed with an equal quantity of sand, it gives a very hard cement. By impregnating plaster-casts with solution of soluble glass, and exposing them to air, they acquire a high degree of hardness.

Gypsum is occasionally used for agricultural purposes; its operation as a manure seems to be due chiefly to its direct necessity to the composition of the plant, for nearly all plant-ashes contain this substance. It has been found advantageous to mix gypsum with dung or stable-manure, since it fixes the carbonate of ammonia, converting it, by double decomposition, into sulphate.

PHOSPHATES OF LIME.

§ 199. Only the tribasic phosphates of this base have received any considerable share of attention.

TRIPHOSPHATE OF LIME ($3\text{CaO}.\text{PO}_3$) is precipitated when chloride of calcium is added to triphosphate of soda ($3\text{NaO}.\text{PO}_3$). It is likewise obtained when chloride of calcium is added to common phosphate of soda ($2\text{NaO}.\text{HO}.\text{PO}_3$), mixed with a little ammonia, or when an excess of phosphoric acid ($3\text{HO}.\text{PO}_3$) is added to chloride of calcium, and followed by excess of ammonia.

The composition of these precipitates is expressed by the formula $3\text{CaO}.\text{PO}_3 + 2\text{Aq}$; they are white, gelatinous, and easily soluble in acids.

The mineral *apatite* is a compound of triphosphate of lime with chloride or fluoride of calcium ($3(3\text{CaO}.\text{PO}_3),\text{CaF}$).

COMMON PHOSPHATE OF LIME ($2\text{CaO}.\text{HO}.\text{PO}_3$).—When common phosphate of soda ($2\text{NaO}.\text{HO}.\text{PO}_3$) is added to chloride of calcium, a white gelatinous precipitate is obtained, of the formula $2\text{CaO}.\text{HO}.\text{PO}_3 + 4\text{Aq}$. This precipitate is easily soluble in acids; when digested with ammonia, it is converted into the triphosphate ($3\text{CaO}.\text{PO}_3$), whilst phosphate of ammonia is found in solution.

ACID PHOSPHATE OF LIME ($\text{CaO}.\text{HO}.\text{PO}_3$) is formed when bone-earth is treated with sulphuric acid; if the former be digested for some time with oil of vitriol, water then added, and the solution filtered from the insoluble sulphate of lime, it yields, on evaporation, crystals of the formula $\text{CaO}.\text{HO}.\text{PO}_3$; these are deliquescent, and very soluble in water. When a large excess of sulphuric acid is added to triphosphate of lime, the whole of the phosphoric acid is liberated.

It will be remembered that the acid phosphate of lime is employed for the preparation of phosphorus.

BONE-EARTH, BONE-ASH.

The residue obtained by the incineration of bones, contains about $\frac{1}{3}$ of phosphate of lime; the formula of this phosphate was formerly written $8\text{CaO}.\text{P}_3\text{O}_8$, being viewed as a combination of $2(3\text{CaO}.\text{PO}_3)$ with $2\text{CaO}.\text{PO}_3$. The recent investigations of Raoult, however, have shown this to be merely triphosphate of lime, $3\text{CaO}.\text{PO}_3$.

Ground bones are frequently employed as a manure, their action depending partly upon the readily decomposable animal matter (gelatin) which they contain, and partly upon the supply of the phosphoric acid so necessary to the com-

position of plants. When ground bones alone are employed, the triphosphate of lime which they contain, being insoluble in water, can only be taken up by the roots of the plants in minute quantities, dissolved by the saline solutions which it meets with in the soil;¹ where an abundant supply of phosphoric acid is needed, as for turnip-crops, it is found more advantageous to convert the triphosphate into the acid phosphate of lime, which is soluble in water. This is effected by gradually mixing the bone-dust with $\frac{1}{3}$ of its weight of oil of vitriol, and adding an equal quantity of water after each portion of oil of vitriol; the mass is allowed to remain in a heap till quite dry, and is then used under the name of *superphosphate*; it consists of a mixture of the animal portion of the bones with acid phosphate and sulphate of lime.

Rose has recently examined certain double phosphates of lime and the alkalis. By igniting mixtures of pyrophosphate of lime with the proper proportions of alkaline carbonates, insoluble compounds were obtained, having the composition corresponding approximately to the formula $MO.2CaO.PO_3$. Similar compounds were obtained by igniting mixtures of pyrophosphate of lime with the alkaline chlorides. These compounds, however, could only be produced in the dry way.

Rose also thinks it probable that a class of soluble double phosphates exists, having the general formula $2MO.CaO.PO_3$ (M representing, as before, an alkali-metal.) The experiments were extended to baryta and strontia, with similar results.

CARBONATE OF LIME, CHALK, $CaO.CO_2$.

§ 200. This substance is found in great abundance, and in numerous forms, in the mineral world. Calcareous spar, Iceland spar, aragonite, limestone, chalk, and marble, all consist of pure carbonate of lime.

Shells are composed chiefly of this substance; the bones of animals likewise contain a considerable quantity. It is also found in spring and river waters.

Carbonate of lime may be prepared artificially by precipitating a solution of chloride of calcium with carbonate of soda, and washing; the *precipitated chalk* of the Pharmacopœia is prepared in this manner.

Iceland spar is found in transparent colorless rhombohedra, of spec. grav. 2.7; these crystals exhibit the property of double refraction, and are therefore in much request for optical experiments. Other kinds of calcareous spar crystallize in the same system.

Aragonite forms rectangular prisms, which are sometimes colorless, and occasionally colored yellow and blue by metallic oxides. Its spec. grav. is 3.75. When heated, a crystal of aragonite is reduced to a number of small crystals, of the same form as those of Iceland spar.²

The different varieties of *marble* owe their various colors chiefly to organic (bituminous) matters, and the oxides of iron. The white Carrara marble is the purest.

Properties.—It will be seen from the above statements respecting Iceland spar and aragonite, that carbonate of lime is a dimorphous substance. When an alkaline carbonate is added to a cold solution of a lime-salt, a bulky precipitate is obtained, which shortly becomes crystalline, and when examined under the microscope, exhibits the rhombohedra of Iceland spar. If, however, a hot solution of a lime-salt be added to a hot solution of carbonate of ammonia, a

¹ Phosphate of lime may also be taken up by the plants, in a state of solution in water containing carbonic acid.

² When waters containing bicarbonate of lime in solution are exposed to a high temperature, the carbonate of lime is deposited in the same crystalline form as aragonite, whilst that which is deposited at the ordinary temperature, presents the same form as Iceland spar.

powder is precipitated, which is composed of minute crystals similar to those of arragonite; if this powder be gently heated, it is resolved into a collection of minute rhombohedra.

When heated to redness, carbonate of lime loses its carbonic acid, and is converted into quicklime; this decomposition is more easily effected in a current of steam or atmospheric air. If carbonate of lime (chalk) be sealed in an iron tube, and heated, it is not decomposed, but may be fused into a mass which, when cool, has a crystalline structure, and much resembles marble.

Carbonate of lime is insoluble in water, but dissolves in a solution of carbonic acid, forming, probably, a bicarbonate of lime. If a stream of carbonic acid be passed through lime-water, the white precipitate produced at first, gradually disappears, and a solution of *bicarbonate of lime* is produced. This solution readily parts with carbonic acid, and deposits carbonate of lime. This change takes place even on exposure to air, and hence, cisterns which contain water rich in bicarbonate of lime, are often coated with a compact incrustation of the carbonate.

The so-called *petrifying springs* in Tuscany and Auvergne, owe their curious properties to the presence of bicarbonate of lime. When any object is exposed to the action of these waters, it becomes incrustated with carbonate of lime.

Stalactites, found in certain caverns, are composed of carbonate of lime, which is deposited in a crystalline state from every drop of water, holding bicarbonate of lime in solution, which drips through the roof; from the spot upon which the drops of water fall, a *stalagmite* often rises to meet the stalactite depending from above.

The solution of bicarbonate of lime also deposits the carbonate when boiled, thus giving rise to an *incrustation* of this salt upon the interior of boilers in which highly calcareous waters are employed (page 121). Carbonate of lime dissolves in all acids which form soluble salts with its base (excepting in hydrocyanic), with evolution of carbonic acid.

When a solution of lime in sugar-water is exposed to the air at a temperature of about 32° F. (0° C.), colorless rhombohedral crystals are deposited, of the formula $\text{CaO} \cdot \text{CO}_2 + 5\text{Aq}$; these lose their water at a comparatively low temperature (80° to 100° F.)

Uses of Carbonate of Lime.—These are very various. Most kinds of stone employed for building purposes are varieties of limestone; marble is also used to a great extent in building and for statuary. Lithographic stones are composed of carbonate of lime.

It will be remembered that *limestone* is the source of quicklime; it is burnt in considerable quantities for agricultural purposes, and is sometimes employed, unburnt, for the mechanical amelioration of soils.

Limestone is also very much used as a flux. Of late years, burnt lime has been substituted, in some furnaces, apparently with considerable advantage.

Chalk is occasionally used in medicine as an antacid; for this purpose, it is prepared by careful levigation. *Toxic preparations* (levigated shells), are merely another form of carbonate of lime.

From what we have said above respecting the uses of quicklime in the preparation of mortars and cements, and the influence which the presence of other substances has upon their quality, it becomes matter of importance that we should be acquainted with the composition of a specimen of limestone before employing it for the preparation of quicklime. For the analysis of limestones, see *Quantitative Analysis, Special Methods*.

A variety of *carbonate of lime and soda* is found in nature, as the mineral *gaylussite*, the formula of which is $\text{CaO} \cdot \text{CO}_2 \cdot \text{Na}_2\text{CO}_3 - 5\text{Aq}$; This mineral is insoluble in water, but if its water of crystallization be expelled by a gentle heat, water will be decomposed, and a mixture of lime and carbonate of soda.

Binoxide of calcium (CaO_2) is obtained as a white hydrate, when binoxide

of hydrogen is added to lime-water; the binoxide is very unstable, easily parting with the second equivalent of oxygen.

CHLORIDE OF CALCIUM, CaCl.

§ 201. This compound is found in most natural waters. It may be obtained by dissolving lime or its carbonate in hydrochloric acid.

Preparation and Properties.—Chloride of calcium is generally prepared from the residue in the retort after the preparation of ammonia; this residue contains chloride of calcium mixed with a slight excess of lime; it is treated with water, filtered, mixed with a slight excess of hydrochloric acid, and evaporated. The concentrated solution, on cooling, deposits large crystals of the formula $\text{CaCl} + 6 \text{Aq}$.

These crystals are colorless and highly deliquescent six-sided prisms. When exposed *in vacuo*, they lose 4 equivalents of water, and become opaque. They fuse very easily in their water of crystallization, and lose 4 equivalents below 392 F. (200° C.), leaving a white porous mass, which readily absorbs water, and is advantageously employed for drying gases. When further heated, all the water is expelled, and the chloride undergoes the igneous fusion. If the fused mass be strongly ignited, with access of air, chloride is evolved, and the residue becomes alkaline, from the presence of lime. Fused chloride of calcium after exposure to light, is phosphorescent in the dark. Anhydrous chloride of calcium combines with water, with evolution of heat, but the hydrated salt gives rise to considerable depression of temperature when dissolved in water. A mixture of crystallized chloride of calcium and snow, or powdered ice, is capable of lowering the temperature to the extent of 82° F. At the ordinary temperature, water dissolves 15 parts of the crystals. A saturated solution boils at 336° F. (169° C.), and is sometimes employed in operations where a bath of this temperature is required.

Anhydrous chloride of calcium dissolves readily in alcohol; if the solution be evaporated, tabular crystals are obtained, containing 59 per cent. of alcohol.

Chloride of calcium is capable of absorbing ammoniacal gas to a very considerable extent, producing, it is said, a compound of the formula $\text{CaCl}_4 \cdot 4\text{NH}_3$.

Uses.—Crystallized chloride of calcium is employed for preparing the solution used as a reagent.

The dried porous mass, obtained by expelling 4 equivalents of water from the crystals, is used for drying gases, and for absorbing the water in the direct determination of this substance, or of hydrogen, in organic analysis.¹

Anhydrous (fused) chloride of calcium is useful for abstracting water from liquid organic substances; thus, in purifying oil of turpentine, it is digested for a day or two with fragments of fused chloride of calcium, and then distilled from them.

Oxychloride of Calcium ($\text{CaCl}_2 \cdot 3\text{CaO}$) may be prepared by boiling hydrate of lime for some time in a concentrated solution of chloride of calcium; the filtered solution, on cooling, deposits prismatic crystals of the formula $\text{CaCl}_2 \cdot 3\text{CaO} + 15\text{Aq}$; these crystals are decomposed by alcohol, or by pure water, into lime and chloride of calcium.

FLUORIDE OF CALCIUM, FLUOR-SPAR, CaF.

This substance is pretty abundant in the mineral kingdom, where it constitutes all the varieties of fluor-spar.

¹ Care should be taken that the chloride employed for this latter purpose be not alkaline (as it sometimes is, from neglecting to add excess of hydrochloric acid in preparing it from ammonia residues), or it will, by absorbing part of the carbonic acid, cause an excess in the hydrogen, and a deficiency of carbon.

Fluor-spar is generally found in veins associated with ores of tin, lead, copper, and zinc.

It will be remembered that fluoride of calcium occurs, associated with phosphate of lime, in apatite.

Fluoride of calcium, in small quantity, enters into the composition of the bones of animals, and is found in some mineral waters.

It is precipitated when a soluble lime-salt is mixed with an alkaline fluoride.

The precipitate is gelatinous, and very transparent, nearly insoluble in acetic acid, and sparingly soluble in hydrochloric.

Properties.—Fluor-spar is found in crystals, the primitive form of which is the cube; these are generally of a yellow or purple color, due to the presence of organic matter; they are sometimes pale green, or even colorless. The specific gravity of fluor-spar is 3.1. When heated, the crystals decrepitate, at the same time emitting a peculiar blue or green light, which resembles a flame playing over the surface. When the decrepitation has ceased, the phosphorescence is no longer perceived, perhaps it is an electric phenomenon. At a high temperature (in the blowpipe-flame) fluor-spar fuses, and becomes crystalline on cooling.

Fluoride of calcium is very sparingly soluble in water; it dissolves to some extent in hydrochloric and nitric acids, with evolution of a little hydrofluoric acid; ammonia precipitates part of the fluoride unchanged from these solutions.

Concentrated sulphuric acid converts it into sulphate of lime, with expulsion of hydrofluoric acid.

Fluoride of calcium is decomposed when fused with alkaline carbonates, yielding carbonate of lime and an alkaline fluoride. It has lately been asserted that this decomposition is not complete unless silica be mixed with the fluor-spar, when an alkaline silicofluoride is formed.

Uses.—Fluor-spar is employed in the laboratory as the source of all other fluorine-compounds. It is used as a flux in smelting certain ores, especially those of copper.

Moreover, considerable quantities of it are employed for the fabrication of ornamental vases, &c. *Derbyshire spar*, so much used for this purpose, is a variety of fluoride of calcium.

SULPHIDES OF CALCIUM.

§ 202. Three sulphides of calcium are known.

Sulphide of Calcium (CaS) is formed when hydrosulphuric acid comes in contact with lime; it may also be obtained by calcining a mixture of sulphate of lime with charcoal.

Sulphide of calcium is a white amorphous substance, which is luminous in the dark;¹ it is very sparingly soluble in water. The solution has an alkaline reaction. When boiled with water, it yields hydrate of lime, and hydrosulphate of sulphide of calcium:—



Suspended in water, and subjected to a current of carbonic acid, it yields carbonate of lime and sulphuretted hydrogen.

An insoluble *oxysulphide of calcium* is formed in the balling process, in making carbonate of soda.

Bisulphide of Calcium (CaS₂) may be obtained by boiling for a few instants a mixture of milk of lime and flowers of sulphur; the liquid filtered while hot, deposits, on cooling, orange-yellow needles of the bisulphide, which are almost insoluble in cold water; their formula is CaS₂ + 3Aq.

Pentasulphide of Calcium (CaS₅) is obtained in solution when milk of lime is

¹ Sulphide of calcium is hence sometimes termed *Canton's phosphorus*.

boiled for a considerable time with a large excess of sulphur. It is needless to say that the formation of the bisulphide and pentasulphide of calcium is attended by that of hyposulphite of lime :—



PHOSPHIDE OF CALCIUM, Ca_2P .

Preparation.—To prepare phosphide of calcium, vapor of phosphorus is passed over quicklime heated to redness.

An earthen crucible of about a pint capacity is taken, and a round hole drilled into the centre of the bottom; into this hole the neck of a Florence flask is luted (with a lute composed of 8 or 10 parts of brick-dust, 1 part of litharge, and linseed oil), so that it may project about half an inch in the interior of the crucible; the apparatus should be allowed to remain for a day or two, that the lute may dry; a small quantity of dry phosphorus is then introduced into the flask, the crucible is filled with fragments of quicklime, and so placed in a furnace that it may be surrounded with redhot coke or charcoal, without heating the phosphorus. When the crucible is heated to redness, a few pieces of redhot charcoal may be placed beneath the Florence flask, and the phosphorus converted into vapor.

The reaction which takes place when vapor of phosphorus is passed over red-hot lime may be expressed by the equation :—



The product of the operation is brown and amorphous. When treated with water, it is decomposed, with evolution of the spontaneously inflammable liquid phosphuretted hydrogen, PH_3 , which resolves itself at once into solid and gaseous phosphuretted hydrogen (see page 181).

The alliaceous odor exhaled by the brown mass is due to the phosphuretted hydrogen produced by the action of atmospheric moisture.

MAGNESIUM.

Sym. Mg. Eq. 12. Sp. Gr. 1.743.

§ 203. This metal, in combination, is found pretty abundantly in nature. It enters into the composition of many minerals, and exists in most natural waters.

Magnesium was first prepared by Bussy, who obtained it by decomposing chloride of magnesium with potassium at a high temperature.

Preparation.—A few pellets of potassium or sodium are placed at the bottom of a platinum crucible, and covered with fragments of anhydrous chloride of magnesium; the cover of the crucible is then secured with iron wire, and the heat of a spirit-lamp applied. A violent reaction takes place, the result of which is expressed by the following equation :—



The crucible is then allowed to cool, and the mass treated with very cold water, which dissolves the chloride of potassium and the excess of chloride of magnesium, and leaves the metal in the form of globules.

This metal has recently been prepared in large quantities by Bunsen, by decomposing fused chloride of magnesium by the galvanic current.

Properties.—Magnesium is a white malleable¹ metal resembling silver.

¹ According to Bunsen, the magnesium obtained by electrolysis is scarcely more ductile than zinc at ordinary temperatures, whilst that reduced by potassium may be ham-

It is not altered by dry air at the ordinary temperature, but is tarnished when exposed to moist air. When heated to dull redness in air or oxygen, it burns with a vivid light, and is converted into magnesia.

This metal fuses at a moderate red heat. It is scarcely affected by pure water at the ordinary temperature, but it decomposes it at the boiling point, evolving hydrogen. Dilute acids readily dissolve this metal, evolving hydrogen, and producing a salt of magnesia.

Nitric acid is entirely deoxidized by magnesium, nitrogen being evolved; the metal takes fire when thrown into dilute nitric acid. Concentrated sulphuric acid dissolves it, with evolution of sulphurous acid.

Magnesium forms only one oxide—magnesia.

OXIDE OF MAGNESIUM, MAGNESIA, MAGNESIA USTA, CALCINED MAGNESIA.

MgO. Eq. 20.

Preparation.—This oxide is generally prepared by calcining the substance termed in pharmacy *magnesia alba* until it ceases to effervesce with acids. *Magnesia alba* is a compound of hydrate and carbonate of magnesia, from which the water and carbonic acid may be expelled at a moderately high temperature.

The magnesia prepared in this way is a very light bulky powder; when a denser kind is required, it is prepared by calcining the heavy carbonate of magnesia, as it is termed; the magnesia thus obtained is known as *heavy calcined magnesia*.

It may also be obtained in a state of perfect purity, by igniting the nitrate of magnesia.

Properties.—Magnesia is a white powder, varying, as already mentioned, in density. It is unaltered by heat, having never yet been fused. Magnesia slowly absorbs water and carbonic acid from the air. When moistened with water, it combines with it, without appreciable elevation of temperature, to form hydrate of magnesia.

HYDRATE OF MAGNESIA, MgO.HO.

Crystallized hydrate of magnesia composes the mineral *brucite*.

It may be prepared directly from anhydrous magnesia, or by decomposing a solution of a salt (sulphate) of magnesia, with potassa.

Properties.—Hydrate of magnesia forms a white powder, which slowly absorbs carbonic acid from the air. Its water is easily expelled by heat. This hydrate is very sparingly soluble in water, but sufficiently so to exhibit an alkaline reaction. 1 part of anhydrous magnesia requires about 5,000 parts of water at the ordinary temperature; it is even less soluble in hot water, 1 part requiring 50,000 parts.

Magnesia is chiefly employed in medicine as an antacid; it is especially useful as an antidote to the mineral acids in cases of poisoning. Magnesia is sometimes administered as an antidote to arsenious acid.

The magnesia salts are generally neutral to test-papers.

NITRATE OF MAGNESIA, Mg(NO₃)₂.

It is found in the mother-liquors of the sulphate refinery.

It may be prepared by dissolving magnesia or its carbonate in dilute nitric acid and evaporating to dryness.

Properties.—The anhydrous substance is rhombohedral prisms of the formula

$Mg(NO_3)_2$. It is soluble in water, and its solution is neutral to test-papers. The hydrate is also soluble in water, and its solution is neutral to test-papers. The anhydrous substance is rhombohedral prisms of the formula $Mg(NO_3)_2$. It is soluble in water, and its solution is neutral to test-papers. The hydrate is also soluble in water, and its solution is neutral to test-papers.

$\text{MgO.NO}_3 + 6\text{Aq}$. It is very soluble in water and alcohol. Nitrate of magnesia is easily decomposed by heat; when exposed for some time to a temperature of 482°F . (250°C .), it is converted into a basic salt, of the formula $2\text{MgO.NO}_3 + 4\text{Aq}$; all the nitric acid is expelled below a red heat.

The *Hypochlorite of Magnesia*, or rather, a mixture of this substance with chloride of magnesium, has lately been applied to the *bleaching of flax* by Clausson, who prepares it by mixing equivalent quantities of sulphate of magnesia and bleach, in solution, when sulphate of lime is deposited, and the clear liquor is drawn off for use.

SULPHATE OF MAGNESIA, EPSOM SALTS, MgO.SO_4 .

§ 205. This salt is sometimes found as an efflorescence on the surface of rocks. It occurs native as the mineral *hair-salt* (*Haar salt*), found as an efflorescence, in some parts of Spain.

Sulphate of magnesia exists in sea-water and in many spring-waters in considerable quantity. In England, the springs at Epsom and Cheltenham are noted for the amount of this salt which they contain. The waters of Sedlitz and Pullna, in Bohemia, also contain considerable quantities of this salt.

Preparation.—Much of the sulphate of magnesia found in commerce is prepared from the mother-liquor (*bittern*) in the separation of salt from sea-water; this mother-liquor is concentrated by evaporation, the crystals of common salt being removed as they are deposited, and the solution allowed to crystallize. The rough crystals thus obtained are called *single Epsom salts*; when purified by another crystallization, they are termed *double Epsom salts*.

Sulphate of magnesia is also sometimes prepared by saturating dilute sulphuric acid with powdered magnesian limestone (*dolomite*, carbonate of lime and magnesia), when the lime is separated as sulphate, and the sulphate of magnesia may be crystallized from the solution.¹ The carbonic acid evolved in the decomposition of the dolomite is employed in the preparation of bicarbonate of soda.

Near Genoa, sulphate of magnesia is obtained from a magnesian shale, containing sulphides of copper and iron. When the shale is roasted and exposed to the action of air and moisture, the sulphur is in great measure converted into sulphuric acid, part of which enters into combination with the magnesia, forming sulphate of magnesia, while the remainder is converted into the sulphates of iron and copper. The mixture is then treated with water, and the liquid is digested with scraps of iron, which precipitate the copper in the metallic state. On adding to the solution a certain quantity of lime, the whole of the iron is precipitated, and sulphate of magnesia (containing traces of iron and copper) may be crystallized from the clear liquor.

Refuse alum-liquors are also employed for the preparation of sulphate of magnesia. These contain, besides sulphate of magnesia, compounds of sulphuric acid with potassa, alumina, and the oxides of nickel, cobalt, and iron; the impure sulphate of magnesia is separated from them by crystallization, and the sulphates of alumina, nickel, cobalt, and iron, contained in this product, are precipitated by a suitable addition of magnesian limestone; the mixture is then dried and roasted, to peroxidize the iron, after which it is ground to powder, treated with water, the solution filtered and evaporated to crystallization.

Properties.—Ordinary sulphate of magnesia occurs in the form of fine needle-like crystals, which are rectangular four-sided prisms; the formula of these crystals is $\text{MgO.SO}_4 \cdot \text{HO} + 6\text{Aq}$. These effloresce slightly in dry air.² When heated, the

¹ The magnesian-limestone is sometimes calcined previously to the treatment with sulphuric acid, and the lime removed, as far as possible, by washing with water.

² Some specimens of the commercial sulphate deliquesce slightly, from the presence of a little chloride of magnesium.

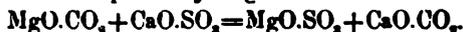
crystals undergo the aqueous fusion, and lose 5 eqs. of water below 212° F. (100° C.); at 270° F. (132° C.) they lose another equivalent of water, but the last equivalent (water of constitution) is not expelled till the temperature rises to 460° F. (238° C.); if further heated, the salt undergoes the igneous fusion, and, at a very high temperature, is decomposed.

Sulphate of magnesia is very soluble in water; at the ordinary temperature, 100 parts of water dissolve 68 parts, and, at the boiling-point, 150 parts of the common crystals. If a hot saturated solution be allowed to cool the crystals which deposit between 77° and 86° F. (25° and 30° C.) have the formula $MgO.SO_3.HO + 5Aq$, and have not the same crystalline form as those with 6Aq; below 77° F., the ordinary crystals are deposited, until the temperature falls below 32° F. (0° C.), when the crystals have the composition $MgO.SO_3.HO + 11Aq$. The reaction of solution of sulphate of magnesia is neutral, and its taste bitter. Sulphate of magnesia is very sparingly soluble in alcohol.

When anhydrous sulphate of magnesia is mixed with carbon and ignited, it leaves a residue of magnesia, not of sulphide of magnesium.

Sulphate of magnesia is decomposed by chloride of sodium; when solutions of these salts are mixed, and exposed to a low temperature, crystals of sulphate of soda are obtained.

The occurrence of sulphate of magnesia in waters may be explained by the action of the sulphate of lime, which these formerly contained, upon the magnesian limestone with which they have come in contact. It is found that if a solution of sulphate of lime is filtered several times through a layer of magnesian limestone, all the lime is replaced by magnesia:—



This reaction may, however, be reversed, for it is found that if carbonate of lime be heated with solution of sulphate of magnesia, to a temperature of 392° F. (200° C.), in a stout sealed glass tube, carbonate of magnesia and sulphate of lime are formed.

Sulphate of magnesia is used extensively in medicine. It is employed in the laboratory as a reagent, and is the source of most other compounds of magnesia.

The sulphate of magnesia of commerce is sometimes adulterated with sulphate of soda.

The water of constitution in sulphate of magnesia is capable of being replaced by an alkaline sulphate, a double salt being thus formed.

The double sulphate of magnesia and potassa, $MgO.SO_3.KO.SO_3 + 6Aq$, is deposited during the evaporation of the mother-liquor from the salt-works.

The formula of the corresponding ammonia-salt is $MgO.SO_3.NH_4O.SO_3 + 6Aq$; it has the same form as the preceding.

PROSPHATES OF MAGNESIA.

§ 206. COMMON PROSPHATE OF MAGNESIA ($2MgO.HO.PO_3$) may be obtained by dissolving basic carbonate of magnesia (magnesia alba) in common phosphoric acid, or by mixing hot concentrated solutions of sulphate of magnesia and phosphate of soda, when the new salt is deposited on cooling. It crystallizes in hexagonal needles of the formula $2MgO.HO.PO_3 + 14Aq$. These crystals lose 8 equivalents of water at the boiling-point, and 14 equivalents at 347° F. (175° C.), at a higher temperature the last equivalent of water is expelled, and the phosphate of magnesia, $2MgO.PO_3$, remains.

Common phosphate of magnesia is sparingly soluble in water, but dissolves easily in acids. If long boiled with water, it is decomposed into free phosphoric acid, and a basic salt of the formula $3MgO.PO_3 + 7Aq$.

Phosphate of magnesia enters into the composition of the bones of animals. This phosphate is said to be $3MgO.PO_3$.

PHOSPHATES OF MAGNESIA AND AMMONIA.

TRIPLE PHOSPHATE ($\text{MgO.NH}_4\text{O.HO.PO}_3$) is sometimes a constituent of urinary calculi.

It may be prepared by adding phosphite of ammonia ($2\text{NH}_4\text{O.HO.PO}_3$) to a hot solution of sulphate of magnesia, when prismatic crystals are deposited on cooling, of the formula $\text{MgO.NH}_4\text{O.HO.PO}_3 + 3\text{Aq}$. When ignited, this salt yields metaphosphate of magnesia (MgO.PO_3).

AMMONIACO-MAGNESIAN PHOSPHATE ($2\text{MgO.NH}_4\text{O.PO}_3$) occurs in the seeds of some of the cereals, and sometimes in the form of calculi. It is also occasionally deposited from urine. The minerals *guanite* and *struvite* consist of this salt. Ammoniaco-magnesian phosphate is precipitated by adding a solution of phosphate of soda to a mixture of sulphate of magnesia with chloride of ammonium and ammonia; it is thus obtained as a white crystalline precipitate (minute four-sided prisms), which is slightly soluble in water, but insoluble in dilute ammonia. Its formula is $2\text{MgO.NH}_4\text{O.PO}_3 + 12\text{Aq}$. By ignition, this salt is converted into pyrophosphate, 2MgO.PO_3 . When heated to 212°F . (100°C .) it loses 10 equivalents of water. The ammoniaco-magnesian phosphate dissolves readily in acids.

Rose has obtained an insoluble *double phosphate of magnesia and potassa* (2MgO.KO.PO_3) by igniting phosphate of magnesia with carbonate of potassa.

CARBONATE OF MAGNESIA, MgO.CO_2 .

§ 207. This salt is found in nature in the pure state as the mineral *magnesite* ($\text{MgO.CO}_2 + 3\text{Aq}$).

Preparation.—The anhydrous carbonate may be prepared artificially, by placing a tube containing solution of carbonate of soda in a strong tube containing solution of sulphate of magnesia, sealing the outer tube hermetically, heating it to 320°F . (160°C .), and inverting it so that the solutions may mix; crystalline grains of the anhydrous carbonate are deposited.

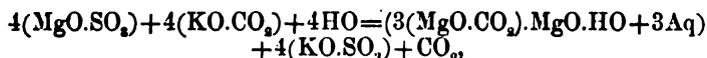
This carbonate is also deposited in crystals, when a solution of bicarbonate of magnesia is evaporated in a current of carbonic acid gas.

Properties.—The native carbonate is occasionally met with in rhombohedral crystals. Magnesite is a white amorphous mineral, very hard, of specific gravity about 2.6. When heated, carbonate of magnesia is easily converted into magnesia. It is insoluble in water, but dissolves in acids, with evolution of carbonic acid.

Carbonate of magnesia dissolves in solution of carbonic acid, probably forming a *bicarbonate*; the solution deposits carbonate of magnesia when boiled. When a solution of bicarbonate of magnesia is exposed to air, a portion of the carbonic acid passes off, and transparent hexahedral crystals are deposited, of the formula $\text{MgO.CO}_2 + 3\text{Aq}$. At a very low temperature, crystals containing 5 eqs. water are deposited. These are very unstable, easily parting with a portion of their carbonic acid, and passing into basic carbonates.

BASIC CARBONATE OF MAGNESIA, SUBCARBONATE OF MAGNESIA. MAGNESIA ALBA, $3(\text{MgO.CO}_2), \text{MgO.HO} + 3\text{Aq}$.

This important compound is prepared by boiling a solution of sulphate of magnesia¹ with a slight excess of solution of carbonate of potassa or of soda for a short time:—



¹ The mother-liquors of the salt-works are sometimes employed for this purpose.

the excess of carbonic acid being expelled as gas; if the mixture were not boiled, the free carbonic acid would retain some carbonate of magnesia in solution. The white precipitate is thrown upon a cloth filter, well washed with boiling water, till the washings give no precipitate with chloride of barium, and dried.

The product thus obtained is a very bulky white powder; it is usually met with in rectangular masses produced by drying it in moulds. It is converted, by a moderate heat, into magnesia.

This substance is very sparingly soluble in cold water, and even less soluble in hot water. It dissolves readily in acids, carbonic acid being disengaged.

The substance known as *heavy carbonate of magnesia*, has the same composition as the above, and is prepared by mixing hot solutions of carbonate of soda and sulphate of magnesia, evaporating to dryness, and washing the residue; the product is much less bulky than the preceding.

When solution of carbonate of soda is added to solution of sulphate of magnesia in the cold, a precipitate of the formula $4(\text{MgO} \cdot \text{CO}_2) \cdot \text{MgO} \cdot \text{HO} + 9\text{Aq}$ is produced; when this is boiled in the solution, it is converted into magnesia alba. This latter is used in medicine for the same purposes as calcined magnesia. Carbonate of magnesia is capable of combining with other carbonates to form double-salts. Thus, we have double carbonates of magnesia and potassa, soda and ammonia.

When a concentrated solution of a magnesia-salt is mixed with an excess of solution of bicarbonate of potassa, and allowed to stand for some days, crystals are deposited of the formula $(\text{KO} \cdot \text{CO}_2 \cdot \text{HO} \cdot \text{CO}_2) \cdot 2(\text{MgO} \cdot \text{CO}_2) + 8\text{Aq}$.

Dolomite is a double carbonate of lime and magnesia, and contains generally single equivalents of these salts, but is often mixed with an excess of carbonate of lime. Since the carbonates of lime and magnesia are isomorphous, the carbonate of magnesia does not alter the crystalline form of the calcareous mineral.²

The *borates of magnesia* possess no practical importance. The mineral *boracite* is found crystallized in cubes, of the formula $3\text{MgO} \cdot 2\text{BO}_2$. A *double borate of magnesia and soda* exists. The mineral *hydroloracite* has the formula $3(\text{MgO} \cdot \text{CaO}) \cdot 2\text{BO}_2 + 9\text{Aq}$.

SILICATES OF MAGNESIA.

Combinations of silicic acid with magnesia are abundant in the mineral kingdom. *Merrillite* is a silicate of the formula $\text{MgO} \cdot \text{SiO}_2 + 2\text{Aq}$; *Steatite* (*sapstone* or *French chalk*) is represented by $5\text{MgO} \cdot \text{SiO}_2 + 2\text{Aq}$. *Chrysolite* and *olivine* have the formula $2\text{MgO} \cdot \text{SiO}_2$. The formula of *peridot* is $3\text{MgO} \cdot \text{SiO}_2$; some specimens are green, from the substitution of oxide of iron for part of the magnesia. *Talc* is a hydrated silicate of magnesia. *Serpentine* is a compound of silicate of magnesia with hydrate of magnesia; it is much used for ornamental purposes, and often possesses beautiful colors due to metallic oxides. *Styrian* and *septulite* are double silicates of lime and magnesia, often colored black or green, from the replacement of the latter by oxide of iron. *Asbestos* or *amiant*, and *talcolite*, are also silicates of lime and magnesia (sometimes containing oxide of iron).

² According to Berzelius, when a very large excess of carbonate of soda is added to a solution of magnesia, a precipitate is obtained, which has the composition $4(\text{MgO} \cdot \text{CO}_2) \cdot \text{MgO} \cdot \text{HO} + 9\text{Aq}$.

³ In the course of an investigation concerning the formation of *dolomite*, it was found that when a mixture of lime and magnesia, or sulphate of magnesia and lumps of powdered calcareous matter, was exposed to carbonic acid gas, a compound of the formula $2(\text{CaO} \cdot \text{CO}_2) \cdot \text{MgO} \cdot \text{CO}_2$, a double salt of carbonate of lime and carbonate of magnesia, was formed, the sulphate of magnesia being converted into sulphate of lime.

CHLORIDE OF MAGNESIUM, HYDROCHLORATE OF MAGNESIA, MgCl.

§ 208. This salt exists in considerable quantity in the mother-liquors of the salt-works, and is formed when magnesia or its carbonate is dissolved in hydrochloric acid. It is also produced when chlorine is passed over a mixture of magnesia with charcoal.

In order to prepare pure anhydrous chloride of magnesium, moderately concentrated hydrochloric acid is saturated with magnesia alba, a considerable excess of chloride of ammonium (in solution) added, and the whole evaporated to dryness, when the residue consists of a double salt of chloride of magnesium and chloride of ammonium; this residue is heated in a platinum dish, when all chloride of ammonium is expelled, and anhydrous chloride of magnesium remains.

The hydrated chloride may be obtained by evaporating the solution of magnesia in hydrochloric acid, and allowing it to crystallize.

Properties.—Anhydrous chloride of magnesium forms white fused masses which deliquesce when exposed to air; it is very soluble in water and alcohol.

The crystallized chloride forms colorless deliquescent needles of the formula $MgCl + 6Aq$; when heated, these evolve water and hydrochloric acid, leaving a residue of chloride of magnesium mixed with a considerable quantity of magnesia:—



so that waters rich in this salt should not be employed for making distilled water, unless lime be added to retain the hydrochloric acid.

Chloride of magnesium forms double salts with the chlorides of the alkali-metals.¹

Sulphide of Magnesium, MgS.—This compound has been but little studied. It cannot be produced by boiling or fusing sulphur together with magnesia. It may be obtained in solution by precipitating sulphate of magnesia with sulphide of barium. When magnesia is suspended in water and saturated with sulphuretted hydrogen, a solution is obtained containing, according to Berzelius, the *hydrosulphate of sulphide of magnesium*, and which, on boiling, deposits a white gelatinous precipitate of sulphide of magnesium.

This sulphide appears to be a sulphur-base.

The properties of magnesia and its compounds show that this base stands between the alkaline earths and the earths proper, much as lithia does between the alkalis and the alkaline earths.

In its alkaline reaction and its relations to carbonic acid, it resembles the alkaline earths (lime, &c.), whilst its behavior with sulphur and the instability of its chloride, give it a similarity to the earths proper (alumina, &c.).

¹ It was found by Clark that when chloride of magnesium was strongly heated in dry ammoniacal gas, it was almost entirely volatilized, a white powder subliming, which had the composition $MgCl + 2NH_3$.

METALS OF THE THIRD GROUP.

ALUMINUM.

Sym. Al. Eq. 13.7.

§ 200. THIS metal, in an oxidized state, is very abundant in nature, a fact which will at once appear when we say that all clays are combinations of alumina with silicio acid.

Wöhler first isolated aluminum by a process exactly similar to that employed for preparing magnesium.

The preparation of this metal is best conducted as follows: A quantity of anhydrous chloride of aluminum is placed in a pretty large platinum crucible, within which is inclosed a smaller crucible containing fragments of potassium; the outer crucible is covered, the lid being secured with wire, and a moderate heat applied; the potassium is thus converted into vapor, which decomposes the chloride of aluminum. The mass is washed with cold water, which leaves only the aluminum.

Care should be taken not to employ an excess of potassium, since solution of potass (produced by the decomposition of water) is capable of dissolving aluminum.

Properties.—The metal is thus obtained as a gray powder, which assumes a white lustre when burnished; its spec. grav. is 2.6. It requires a high temperature for fusion, and is afterwards malleable.

Aluminum is unaltered by exposure to air at the ordinary temperature, but when heated in air or oxygen, is rapidly oxidized and converted into alumina. Water is not decomposed by this metal, at the ordinary temperature, and is slowly acted on even at the boiling point.

Aluminum decomposes water with facility in presence of free acids or alkalis, hydrogen being evolved, and a compound of alumina formed.

Only one combination of this metal with oxygen is known.

SEVERAL VARIETIES OF ALUMINA. ALUMINA.

Al₂O₃ Eq. 27.4.

It is worth as we have before remarked is abundant in nature; it not only occurs in combination with silica and, in some instances, mica, &c., but is often found in the pure state. The mineral structure consists of nearly pure alumina.

Crystallized alumina, colored with various oxides, forms different varieties of precious stones. The ruby, sapphire, emerald, and topaz consist of nearly pure alumina. The emerald is chiefly formed of alumina combined with silicic acid.

Preparation.—Crystallized alumina may be prepared by calcining ammoniacal sulphate, or alumina and ammonia at a very high temperature; the alumina thus prepared retains generally a little sulphuric acid.

Properties.—Alumina in its native state, as corundum, is a very hard mineral (standing next to the diamond, in this respect), of spec. grav. about 4. An opaque variety of this mineral, containing a considerable amount of iron, is known as *emery*, which, when ground and separated by levigation into different degrees of fineness, is much used for polishing.¹

Alumina is obtained artificially as a perfectly white substance, which is not altered by exposure to the highest temperature of a furnace; it may, however, be fused, and become very liquid, in the flame of the oxyhydrogen blowpipe, and this circumstance has been taken advantage of for the preparation of artificial gems by fusing the alumina with traces of metallic oxides.

When exposed to air, alumina is capable of absorbing a considerable quantity of water, but it does not form a hydrate even when moistened. It is quite insoluble in water, and dissolves with difficulty in the strong mineral acids and in caustic alkalies; if it be fused with hydrate of potassa or of soda, the fused mass dissolves entirely in water. Anhydrous alumina adheres very tenaciously to the tongue.

The relations which alumina exhibits to acids and to other bases are somewhat remarkable: it appears to be a weak base, for it does not combine with very weak acids, and is not capable of completely neutralizing the stronger acids; on the other hand, it combines with very strong bases, as will be presently seen, to form crystallizable compounds presenting the characters of salts; hence it would appear that alumina stands on the limit between the two classes, comporting itself as an acid towards strong bases, and as a base with strong acids.

HYDRATES OF ALUMINA.

There are several hydrates of alumina. The mineral known as *diaspore* is a crystallized hydrate of alumina, having the formula $Al_2O_3 \cdot 2HO$.

Hydrate of Alumina ($Al_2O_3 \cdot 3HO$) is prepared by adding an excess of carbonate of ammonia to a solution of alum (sulphate of alumina and potassa), heating for a few minutes, collecting the precipitate on a filter, and well washing with hot water; this precipitate, however, still retains some sulphuric acid; in order to obtain it perfectly pure, it should be redissolved, as far as possible, in hot hydrochloric acid, and the solution reprecipitated with excess of ammonia; the precipitate is washed till free from chlorine, and dried by a gentle heat.

Properties.—Hydrate of alumina is a very bulky gelatinous precipitate, which shrinks very much on drying to a mass resembling gum. Its water is not entirely expelled below a red heat. It does not affect test-papers. The freshly precipitated hydrate is sensibly dissolved by water or by solution of ammonia; indeed, if a considerable excess of the latter be added to a dilute solution of alumina, no precipitate is obtained; but this solubility is much diminished by the presence of chloride of ammonium, so that, by adding a considerable amount of this salt before adding ammonia, we may insure the complete precipitation of the hydrate. The precipitate is easily redissolved by acids and fixed alkalies; but if the precipitate produced by ammonia in solution of alum be collected on a filter and washed, it cannot be entirely redissolved in hydrochloric acid.

Hydrate of alumina has a great affinity for most coloring matters, forming compounds which are termed *lakes*. Thus, if a solution of alum be mixed with an infusion of *logwood*, and an excess of carbonate of potassa be then added, the hydrate of alumina will form, with the coloring matter, a purplish-red lake,

¹ J. Lawrence Smith has recently determined the effective hardness of different varieties of emery; he found that, *ceteris paribus*, those emeries which contained the least water were the hardest. In addition to alumina, oxide of iron, and a little water, the specimens were found to contain silica, lime, and sometimes small quantities of iron-pyrites, titanate acid, and the oxides of zirconium and manganese.

which leaves the solution colorless. This property is turned to advantage in calico-printing, where the compounds of alumina are largely used as *mordants*. The chief aluminous mordant is the acetate, which is decomposed by a boiling heat, with precipitation of a basic acetate, capable of combining with coloring matters; hence, if a pattern be printed in acetate of alumina, and the stuff be then steeped in a hot color-bath, the basic acetate will be precipitated in the fibres, and will fix the color there.

Aluminate of Potassa, $\text{KO} \cdot \text{Al}_2\text{O}_3$.—This compound may be obtained in white granular crystals, by slowly evaporating a solution of alumina in potassa. The crystals have a sweet taste, and a strongly alkaline reaction.

A solution of alumina in potassa is sometimes used as a mordant.

The *Aluminate of Magnesia*, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, is found as a very hard mineral, termed *spinelle*; it crystallizes in octohedra.

Nitrate of Alumina ($\text{Al}_2\text{O}_3 \cdot 3\text{NO}_3$) is prepared by dissolving alumina in nitric acid; it may be obtained from an acid solution in colorless oblique rhombic prisms, containing eighteen eqs. of water. The crystals are very deliquescent and soluble.

SULPHATE OF ALUMINA, $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3$.

§ 210. This salt is occasionally found native, when it is sometimes termed *hair-salt*.

Preparation.—It is usually prepared from clay, as free from iron as possible. The clay is calcined at a dull red heat, reduced to a fine powder, and mixed with half its weight of sulphuric acid of spec. gr. 1.45. The mixture is heated till the acid begins to go off, then left to itself for a day or two; after this time it is extracted with water, when a solution is obtained, containing sulphate of alumina and sulphate of sesquioxide of iron. The solution is now mixed with a solution of ferrocyanide of potassium¹ (yellow prussiate of potassa), as long as any blue precipitate (sesquiferrocyanide of iron, Prussian blue) is obtained, and the filtered liquid, which is now free from iron, evaporated to a syrupy consistence, and allowed to solidify in shallow leaden pans.

Properties.—The sulphate thus obtained is a white mass, which resists a high temperature without decomposition. It is very soluble in water, requiring only twice its weight for complete solution, but very sparingly soluble in alcohol. The aqueous solution has a sweet astringent taste, and an acid reaction; a hot saturated solution, on cooling, deposits small tabular crystals, of the formula $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 + 15\text{Aq}$.

These crystals fuse when heated, intumescence greatly, and are ultimately decomposed, losing the greater part of their acid. Sulphate of alumina is extensively used as a mordant.

A *Basic Sulphate of Alumina*, of the formula $2\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3$, may be obtained by digesting a solution of the neutral sulphate with hydrate of alumina. It has not been crystallized. Another basic sulphate occurs in nature, in the mineral *alunite* ($\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 2\text{Al}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$). It may be prepared by adding a little ammonia to a solution of the neutral sulphate, when it falls down as a crystalline precipitate.

Sulphate of alumina is capable of combining with the sulphates of the alkalis, giving rise to certain double salts, which may be taken as the types of the class of salts termed *aluns*.

AN *Alun* is a double salt, composed of a sulphate of a protoxide combined

¹ On the large scale, ferrocyanide of potassium is commonly employed; the precipitated Prussian blue is then washed, decomposed with a solution of caustic soda, in order to reproduce the ferrocyanide solution, which is used to precipitate a fresh portion of iron.

with the neutral sulphate of a sesquioxide, thus the general formula of an alum may be written:—



where MO represents the basic protoxide, and M_2O_3 the basic sesquioxide.

The alums all crystallize in cubes or octohedra containing 24 eqs. of water.

In order to render the above definition more intelligible, we subjoin the formulæ of some of the principal alums:—

Potash-alum	$KO.SO_3, Al_2O_3.3SO_3 + 24Aq$
Soda-alum	$NaO.SO_3, Al_2O_3.3SO_3 + 24Aq$
Ammonia-alum	$NH_4O.SO_3, Al_2O_3.3SO_3 + 24Aq$
Potash-iron-alum	$KO.SO_3, Fe_2O_3.3SO_3 + 24Aq$
Soda-manganese-alum	$NaO.SO_3, Mn_2O_3.3SO_3 + 24Aq$
Ammonia-chrome-alum	$NH_4O.SO_3, Cr_2O_3.3SO_3 + 24Aq$

SULPHATE OF ALUMINA AND POTASSA, POTASSA-ALUMINA-ALUM, COMMON ALUM, $Al_2O_3.3SO_3, KO.SO_3 + 24 Aq.$ ¹

§ 211. This salt exists native in the neighborhood of Naples, where it is extracted by simply treating the rock with water.²

It may be prepared by mixing together hot concentrated solutions of sulphate of alumina and sulphate of potassa, when crystals of alum are deposited as the solution cools.

In Italy, alum is prepared from *alum-stone*, which is found at Tolfa, near Civita-Vecchia. The composition of this mineral is $KO.SO_3, 3(Al_2O_3.SO_3) + 9Aq$; when this mineral is calcined, a portion of the alumina is converted into the insoluble form; and when the mineral is afterwards treated with water, a quantity of alum is dissolved out;³ the washings are evaporated, when they yield cubical crystals of alum; these crystals have a reddish color, from the presence of a little sesquioxide of iron in the insoluble state (?). This variety of alum is known as *Roman alum*, or *Roch alum*, and is preferred by dyers, since its aqueous solution is always free from iron. It is at present prepared artificially, by mixing solution of alum with a small quantity of carbonate of potassa, which precipitates any sesquioxide of iron which may be present, evaporating to crystallization, and coloring the crystals thus obtained with brick-dust, or Armenian bole, to make them appear like true Roman alum.

Alum is, however, most extensively prepared from *alum slate*, or *shale*, which is a mineral of very common occurrence. Alum slate contains silicate of alumina, together with finely-divided iron-pyrites, and more or less bituminous matter.⁴ The mineral is coarsely broken up, and subjected to a process of oxidation, which generally consists either in exposing it to the continued action of air and moisture, or in throwing it into pyramidal heaps, with or without an additional quantity of combustible, and setting fire to these in different parts, letting them smoulder away till all the pyrites are oxidized. The produce is better, the more slowly and uniformly this operation is conducted. The roasted heaps are then allowed to remain exposed to the air till they are in a fit state for extraction.

¹ According to Jacquelin, 22Aq.

² The natural formation of alum may be easily explained, where iron-pyrites occurs associated with feldspathic rocks; the oxidation of the iron-pyrites (FeS_2) gives rise to sulphate of iron and free sulphuric acid, which combines with the alumina and potassa contained in the feldspar.

³ The calcination of the mineral continues until sulphurous vapors begin to pass off; the mineral is then transferred to cisterns, and repeatedly moistened with water during 3 or 4 months, when it crumbles down to a sort of mud.

⁴ Alum-earth differs from alum-slate more in its texture, which is soft and friable, than in its composition.

Sometimes the heaps take fire spontaneously from the heat evolved by the oxidation of the pyrites; the workmen then smother the fire, to prevent loss of sulphur in the form of sulphurous acid.¹

The alum-shale is often associated with so much coal, that any further addition of fuel to the heaps is found unnecessary; indeed, in some cases, it is requisite to add a certain quantity of shale which is poor in coal, in order to economize the fuel.

The change which takes place during the oxidation is easily intelligible.

The iron-pyrites is converted into sulphate of iron, whilst the excess of sulphur yields a quantity of free sulphuric acid:²—



The latter, acting upon the silicate of alumina, gives rise to sulphate of alumina. The sulphate of alumina and sulphate of iron are then extracted by water,³ and the solution evaporated to the requisite degree of concentration.

The principal substances contained in the crude alum-liquor are, sulphates of alumina, iron, magnesia, and soda, together with small quantities of the sulphates of manganese, potassa, and lime, the chlorides of magnesium and aluminum, mesoquichloride of iron, and free sulphuric and hydrochloric acids. The liquor always contains a certain amount of potassa-alum (the potassa being derived from the shale itself, or from the wood employed as fuel) and of ammonia-alum (unless too high a temperature has been employed in the process of oxidation, the ammonia being derived from the destructive distillation of the coal).

The crude alum-liquor generally contains a sufficient amount of green vitriol (sulphate of iron) to pay for extraction, hence the manufacture of this salt is usually carried on simultaneously with that of alum. Any persalt of iron which the liquor may contain is reduced by metallic iron, and the solution is then boiled down to the point at which the green vitriol crystallizes out. In this manner a mother-liquor is obtained, which is saturated with sulphate of alumina. The green vitriol is purified by recrystallization.

The liquor is now mixed with a strong solution of chloride of potassium,⁴ which converts the sulphates (with the exception of sulphate of alumina) into chlorides, which, being much more soluble, are more easily removed from the resulting alum than the sulphates could be. The due regulation of the amount of chloride of potassium added, is of considerable importance, since an excess of that salt would give rise to the production of chloride of aluminum.

The solution of the chloride is gradually added to the liquor, with constant agitation, and the alum that thus produced is then allowed to subside; it is afterwards drained, and washed with a little cold water. It is then redissolved, by exposing it in a perforated wooden frame, to the action of steam, and the saturated solution thus obtained is allowed to flow into wooden casks, or roach-

¹ It was first observed that the sulphuric acid which is produced in these parts of the heap is less than the quantity of sulphur which is absorbed by the alumina, and subsequently discovered that sulphuric acid, by the sulphate of iron, is formed on exposing the alum-shale to the air.

² A certain quantity of sulphuric acid is also formed in consequence of the formation of sulphate of iron, which is a persalt, and the persalt is oxidized by exposure.

³ The alum-shale is often associated with the heaps of exhausted iron, which retains a quantity of sulphuric acid, and the alum-shale is often associated with the iron.

⁴ The quantity of potassium chloride which is added to the liquor, according to the nature of the liquor, varies from 10 to 20 per cent.

⁵ The alum-shale is often associated with the heaps of exhausted iron, which retains a quantity of sulphuric acid, and the alum-shale is often associated with the iron.

⁶ The alum-shale is often associated with the heaps of exhausted iron, which retains a quantity of sulphuric acid, and the alum-shale is often associated with the iron.

⁷ The alum-shale is often associated with the heaps of exhausted iron, which retains a quantity of sulphuric acid, and the alum-shale is often associated with the iron.

The mother-liquor from the alum-crystals receives different applications, depending upon its composition. If it contain much sulphate of iron, it is digested with metallic iron, to neutralize any free sulphuric acid, and to deoxidize any persulphate of iron, and green vitriol is then crystallized from it. If much chloride of iron be present, the liquor is evaporated to dryness, and heated to redness, when sesquioxide of iron is left, which is employed as a pigment. The mother-liquors are also sometimes employed for the preparation of sulphate of ammonia, from the ammoniacal liquor of the gas-works, or, when they contain much magnesia, for the manufacture of Epsom salts.

[In some places, alum is manufactured by allowing the sulphurous acid, produced in metallurgic operations, to act upon rocks containing alumina, in the presence of air and moisture, thus giving rise to sulphate of alumina, from which alum may be manufactured, in the manner above detailed. Alum is also made from clay, which is converted into sulphate of alumina by a process which has already been described (§ 210). It has been proposed to manufacture alum from feldspar, by fusing it first with sulphate, and afterwards with carbonate of potassa; when the resulting mass is boiled with water, an insoluble silicate of alumina and potassa is left, which is converted into alum by treatment with sulphuric acid.]

Properties.—Alum is found in commerce in large octohedral crystals, the angles of which are sometimes truncated by the faces of a cube; these crystals are frequently aggregated in large masses, which retain the form of the casks in which the crystallization has taken place.

The crystals of ordinary alum are colorless, but those of Roch alum have (as before mentioned) a brownish-red color. They are somewhat efflorescent in dry air.¹ When heated to 198° F. (92° C.), they undergo the aqueous fusion, and when further heated, lose their water with very considerable intumescence, yielding a spongy mass, which is known as *burnt alum* (*alumen exsiccatum vel ustum*). A high temperature is required to expel the whole of the water; even at 392° F. (200° C.) a small quantity of water remains. Alum, which has been heated to this temperature, redissolves with difficulty in water. At a much higher temperature, the salt itself is decomposed, sulphurous acid and oxygen are disengaged, and a mixture of alumina and sulphate of potassa remains.²

The crystals dissolve in about ten parts of water at 50° F. (10° C.), and in less than one-third of their weight at the boiling-point, so that a hot saturated solution of alum deposits the greater part in crystals, on cooling.

The solution of alum has an acid reaction and a sweetish astringent taste.

If alum be dissolved in hot concentrated sulphuric acid, crystals are deposited on cooling, of the formula $Al_2O_3 \cdot 3SO_3 \cdot KO \cdot SO_3 + 3Aq$.

When potassa or its carbonate is gradually added to a solution of alum, until the precipitate which is formed is no longer dissolved on stirring, the liquid, when evaporated, gives cubical crystals, which have been noticed above as artificial Roman alum. These crystals are generally supposed to have the same composition as those of ordinary octohedral alum, but it has been asserted that they consist of a basic alum, which is very probable, since, when their solution is boiled, it deposits a white precipitate, and the filtered liquid, on evaporation, deposits octohedra of common alum.

If an intimate mixture of alum with carbon or sugar be calcined in a close vessel as long as any inflammable gas (carbonic oxide) is evolved, the residue will consist of a mixture of alumina, charcoal, and sulphide of potassium in a very finely-divided state. In consequence of the rapid oxidation of the last-

¹ According to Hertwig, alum loses 10 eqs. of water at 212° F. (100° C.).

² If a very intense heat be employed, a compound of alumina and potassa is left.

mentioned substance, the mixture takes fire when thrown into the air, and has hence received the name of *Homborg's pyrophorus*.

Uses of Alum.—This salt is very largely employed in dyeing and calico-printing, in paper-making, in the manufacture of colors, in rendering wood and paper incombustible, and in medicine.

For the first three of these uses, the presence of iron in a soluble form in the alum would be very injurious. Iron may be easily detected by mixing the solution of alum with ferrocyanide of potassium, which would produce a blue precipitate.

A sulphate of alumina and potassa having the same composition as the mineral *alum-stone*, viz., $\text{KO.SO}_3, 3(\text{Al}_2\text{O}_3.\text{SO}_3)+9\text{Aq}$, may be obtained as a crystalline precipitate by boiling a solution of alum with freshly-precipitated hydrate of alumina.

Soda-alum is much more soluble in water than potassa-alum. Like this salt, it is sometimes found native.

Ammonia-alum, which also occurs native, may be prepared by the direct combination of sulphate of alumina with sulphate of ammonia. On the large scale, ammonia-alum is prepared by processes similar to those employed in the manufacture of potassa-alum. It is very similar in its properties to potassa-alum; when ignited, it leaves a residue of alumina.

Phosphate of Alumina occurs in nature as the mineral *wavellite*, the formula of which is $3\text{Al}_2\text{O}_3.2\text{PO}_5+12\text{Aq}$. Hermann has recently shown that the mineral *gibbsite*, formerly supposed to be a hydrate of alumina, is really a phosphate, the presence of the phosphoric acid having been overlooked by other analysts, in this mineral, as, at an earlier period, it was overlooked in *wavellite*. The formula of *gibbsite* is $\text{Al}_2\text{O}_3.\text{PO}_5+8\text{Aq}$.

The precipitate produced by common phosphate of soda in solution of alum, formerly supposed to be $\text{Al}_2\text{O}_3.\text{PO}_5$, has been found by Ludwig to contain $8\text{Al}_2\text{O}_3.9\text{PO}_5$. On dissolving this precipitate in hydrochloric acid, reprecipitating by ammonia, and igniting the washed precipitate, the compound $\text{Al}_2\text{O}_3.\text{PO}_5$ was obtained.

The existence of a *carbonate of alumina* is not certainly established. The precipitate produced by alkaline carbonates in solutions of alumina is generally considered as a hydrate, since its formation is attended with disengagement of carbonic acid.¹

SILICATES OF ALUMINA.

§ 212. Combinations of alumina with silicic acid are very abundant in nature. The minerals known as *andalusite*, *cymrite* (*disthene*) and *sillimanite*, are silicates of alumina of the formula $3\text{Al}_2\text{O}_3.2\text{SiO}_2$. *Allophane* is the hydrate of this silicate.

The *feldspars* form a most important class of minerals, of which the neutral silicate of alumina $\text{Al}_2\text{O}_3.2\text{SiO}_2$ is always a constituent: indeed, the feldspars occupy much the same position among the silicates as the anhydrous alumina-alums occupy among the sulphates: for they consist of silicate of alumina combined with an alkaline silicate, or with silicate of lime or magnesia.

Plow's feldspar (*orthoclase, adularia*) is represented by the formula



This is the most common of the feldspars: it is found in very hard oblique

¹ According to Alagon, the formula of the precipitate produced by carbonate of ammonia is $\text{Al}_2\text{O}_3.\text{CO}_2.\text{H}_2\text{O}$.

prisms, of spec. grav. about 2.5; it fuses to a milky glass at a very high temperature.

Soda-feldspar is usually called *albite*; *lithia-feldspar*, *petalite* (*triphane*, *spodumene*), and *lime-feldspar*, *labradorite* (*anorthite*).

A feldspar exists containing both soda and potassa (*potash-albite*, *pericline*).

Garnet and *stilbite* are double silicates of alumina and lime.

Pumice-stone consists almost entirely of silicate of alumina.

Mica is a double silicate of alumina and potassa, the latter being often replaced by lime or oxide of iron.

Hornblende contains silicate of alumina combined with silicates of lime, magnesia, and oxide of iron.

Basalt is composed of *pyroxene* (silicate of lime, magnesia, and oxide of iron,) and *labradorite* (silicate of alumina, lime, and soda).

Granite is made up of three minerals, quartz, feldspar, and mica.

Gneiss contains the same constituents as granite, but differs from it in structure.

The *clays*, which are also very important members of the mineral kingdom, consist of hydrated silicates of alumina.

Kaolin, which is the purest kind of clay, and serves for the fabrication of fine porcelain, consists chiefly of a silicate having the formula $Al_2O_3, SiO_2, 2Aq$. This substance is formed by the disintegration of feldspathic rocks (granite, for example) under the influence of moisture, when the feldspar is decomposed into basic silicate of alumina (kaolin), and alkaline silicates, which are dissolved by the water.¹

Kaolin is found in white amorphous masses, sometimes containing crystals of unaltered feldspar. A considerable quantity of this clay is found at Saint-Yrieix, near Limoges, and at St. Austle, in Cornwall.

The best china-clay used in England is prepared in Cornwall, by washing decomposed granite with a stream of water, which is then run into reservoirs, where it deposits a sediment, which is afterwards exposed to the air for several months before being used for the manufacture of porcelain.

The composition of common clays is very similar to that of kaolin, but they are generally mixed with more or less sand, feldspar, sesquioxide of iron, carbonates of iron and lime, and organic matter.

When these impurities are present only in small quantity, the clay is termed *fat clay*, from its superior plasticity. Some clays contain as much as $\frac{1}{4}$ per cent. of potassa.

Perfectly pure silicate of alumina is infusible at the highest temperature of our furnaces, but clays containing carbonate of lime and oxides of iron are more or less easily fusible, according to the proportions in which these substances are present.

On the application of a moderate heat, clay loses its water, and shrinks to a dense hard mass. When exposed to a very high temperature, it is converted into a hard sonorous mass, which is still so porous as to absorb water with avidity. The density of the mass is greatest at a low red heat, and is diminished by the application of a higher temperature.

Dilute acids have scarcely any action upon clay. Even concentrated nitric and hydrochloric acids decompose it slowly, dissolving the alumina. Concentrated sulphuric acid, however, attacks it readily, at a high temperature. Clays are generally more readily acted upon by acids when they have been exposed to a moderate heat, but if strongly calcined, they are rendered more refractory.

Solutions of the alkalis scarcely act upon clay, but if it be fused with the alkalis or their carbonates, it is converted into soluble silicates and aluminates.

¹ Brongniart and Malaguti have succeeded in decomposing feldspar by electricity.

Pipe-clay is nearly pure silicate of alumina.

Potter's-clay contains a considerable amount of iron.

Fire-clay, when burnt, yields a very porous mass, which is particularly adapted to resist high temperatures.

Loom is a very impure variety of clay, employed for brick-making.

Ochres are merely clays colored with the oxides of iron and manganese.

Yellow-ochre contains the hydrated sesquioxide of iron, and probably the carbonate of protoxide, both which (the latter with absorption of oxygen and expulsion of carbonic acid) are converted by calcination into anhydrous sesquioxide of iron, thus yielding *red ochre*.

The colors known as *umber* and *sienna* are merely clays colored by the peroxide of iron and manganese.

Bole is also a variety of ochre.

Fuller's earth is a clay of a particular kind, which, when dried, is highly capable of absorbing grease from woollen fabrics, and is employed for this purpose.

Marl is a term applied to clay which contains a considerable quantity of carbonate of lime.⁴

The method to be followed in the analysis of clays is quite the same as that recommended in the case of the insoluble residue of a limestone (see Quantitative Analysis, Special Methods).

EARTHENWARE AND PORCELAIN.

§ 213. We need not say that the chief use of clay is in the manufacture of pottery; and though a complete description of the processes which this art involves is exceedingly interesting, it would be beside our purpose to do more than enter into its leading chemical features.

Though perfectly pure clay possesses a high degree of plasticity, it is nevertheless not well fitted for the manufacture of porcelain, since it shrinks very much, and often cracks in baking; it is therefore necessary to mix it with some substance which shall prevent these effects from becoming apparent; the materials generally employed for this purpose are silica in various forms, feldspar, chalk, bone-ash, and heavy-spar (sulphate of baryta).

It has been already stated that perfectly pure clay is infusible in the kiln, whilst lime, magnesia, and the oxides of iron render it fusible with difficulty, and potassa and soda give it a high degree of fusibility. An excess of iron or lime in the clay may be corrected by an addition of sand.

Clays containing iron (which is usually present as carbonate of the (prot-)oxide) become yellow or red when burnt, the iron being converted into sesquioxide. If the clay have a blue or gray color, due to the presence of organic matter, the color will be destroyed by burning. When fragments of vegetable matter (wood, straw, &c.) are present in the clay, they are very carefully picked out before it is employed for the manufacture of earthenware, since they leave a space when the ware is burnt. Vessels made of ordinary clay are porous, and allow of the passage of fluids; in order to prevent this, they are covered with a glaze, which rises at the temperature of the kiln, and renders the ware impervious.

In the manufacture of earthenware and earthenware, the glaze is of a nature to be elevated by the heat of the kiln, and to spread over the surface; whilst, in the common ware, the glaze is of a nature to spread over the surface, as can be easily seen by the appearance of the ware when it is first fired.

The glaze is usually composed of silica and alumina, and in any particular ware, care is always taken to select such materials as will bear the heat of the kiln, and shall not be very different in expansion from the ware to which they are applied, otherwise numerous

⁴ See also the use of marl in the mechanical amelioration of soils.

cracks, due to unequal contraction in cooling. The glaze may be either transparent or opaque, the latter being generally the case with coarser wares, the imperfections of color being thus concealed.

The chief transparent glazes are feldspar, common salt, the alkalis, boracic acid, silicate of lead, &c.; whilst binocide of tin and phosphate of lime furnish opaque glazes.

The glaze is sometimes colored with a metallic oxide. The number of colors which can be applied in this way is very limited, since few are capable of resisting the high temperature to which the ware is exposed.

A *blue* color is usually imparted by cobalt; a *green* by chromium; *brown* is obtained with iron and manganese; the *yellow* with titanium; and *black* with uranium.

The *finer colors* are actually painted on the baked ware, and are of such a nature that they may be burnt in, at a moderately high temperature, in a muffle.

These colors consist of certain fluxes (fusible glasses) colored with metallic oxides, and are generally ground up with volatile oils, and laid on with a brush. The chief ingredients of the fluxes are sand, feldspar, borax and boracic acid, nitre, alkaline carbonates, litharge and red lead, and teroxide of bismuth. (See p. 225.)

A *blue* color is obtained with cobalt; *green* with sesquioxide of chromium or oxide of copper; *yellow* with sesquioxide of uranium, chromate of lead, sesquioxide of iron, antimonie acid, and silver. *Red* is imparted by suboxide of copper or sesquioxide of iron.

Violet and *rose* tints are produced by purple of Cassius; *black* by uranium, or a mixture of oxides of cobalt and manganese.

The *white enamel* is given by binocide of tin, phosphate of lime, or a mixture of oxides of antimony (p. 226.)

A *golden lustre* is imparted by fulminating gold, painted on with turpentine, and burnt in the muffle; the lustre of the metallic gold thus obtained is improved by burnishing.

We shall now proceed to notice a few of the chief points of interest in the chemical history of the different results of the ceramic art.

Refractory bricks, which are employed for lining the interior of furnaces, are composed of plastic clay containing no gypsum, carbonate of lime, nor oxides of iron; hence good refractory bricks are nearly white.

Crucibles are, of necessity, made of a material which is capable of resisting a very high temperature; the most refractory crucibles are termed *black-lead crucibles*, and are made from a mixture of clay and graphite. *Hessian crucibles* are made of a mixture of clay and sand; their porosity is a great disadvantage.

The materials employed in the manufacture of *English porcelain*, in addition to clay, are bone-ash, flints, Cornish stone, carbonate of soda, borax, and binocide of tin. The use of the bone-ash and flints must obviously be explained for mechanical reasons, while the carbonate of soda and borax act as fluxes to give greater coherence to the ware, and the binocide of tin improves its color and appearance.

A *frit* is generally prepared by moderately heating a mixture of Cornish stone (composed chiefly of quartz and feldspar), flint, soda, borax, and binocide of tin; this frit is then intimately mixed with the *mass*, composed of plastic clay, kaolin, Cornish stone, flint, and bone-ash, and the whole is ground with water to a homogeneous paste, from which the goods are made. These are then *fired* in a kiln or oven, during about forty-eight hours, at a gradually increasing heat, after which they are allowed to cool slowly, and glazed. The glaze is composed of flint, chalk, Cornish stone, borax (and sometimes white-lead); it is applied to the *biscuit* (or baked ware) in a state of uniform mixture with water; the ware is then fired for a shorter time, and at a lower temperature than before, in order to fuse the glaze.

Fine porcelain, or china, is made from a paste of the purest materials; this paste consists of kaolin, or pure plastic clay, and of feldspar, sand, chalk, or gypsum, and sometimes of a mixture of these substances. The paste which is employed at Sévres consists of

Silica	58.5
Alumina	34.5
Lime	4.0
Potassa	3.0

100.0

This porcelain may be said to consist of two parts, the plastic material (kaolin), and the vitreous flux (feldspar, chalk, quartz, and gypsum). The former, which by itself would yield a porous opaque mass, becomes impregnated with the flux, which at once renders it impermeable and translucent.

Since the materials employed are somewhat variable in their composition, an analysis of each is usually made, and the mixture is then proportioned, so that its composition may be expressed by the numbers given above.

The glaze consists chiefly of feldspar, or sometimes of a mixture of feldspar with gypsum, or with some of the dried paste which forms the material itself. This glaze, being very similar in composition to the flux, contracts a very firm adhesion with the ware, and is not liable to crack or scale off. Since this glaze contains no lead (*see* Glass), it is very hard, and is not easily scratched by a knife. Much depends upon the degree of fusibility of the glass; if it be not sufficiently fusible, it does not acquire an even surface; and if, on the other hand, its fusibility be too great, it will be entirely sucked into the ware, leaving the surface rough.

When the ingredients (kaolin and flux) have been prepared by levigation and intimately mixed, the paste has to be reduced to the consistence proper for working, for which purpose, a great part of the water must be expelled. If this were effected by heat, the plasticity of the material would be much impaired, to avoid which, the paste is either run into boxes, the bottoms of which are composed of gypsum, to absorb the water, or it is pressed in linen bags, or thrown upon a filter made of felt, placed upon a funnel from which the air may be exhausted, when the superfluous water is forced through by atmospheric pressure. The mass is next kneaded, to render it perfectly uniform, and stored away for a year or so in a moist place; it then evolves an odor of sulphuretted hydrogen, due to the action of the traces of organic matter upon the sulphate of lime, and its plasticity becomes greatly improved, probably from the alteration of texture which must result from the evolution of gaseous products of the putrefaction of the organic matter. The paste is then fit for working. The moulds employed to assist in forming the vessels are usually made of gypsum, which absorbs the water. The goods are dried by mere exposure to the air, since rapid drying would destroy them.

The vessels are fired once, as mentioned above, before glazing. The glaze is usually mixed to a thin slip with water containing vitriol, which prevents the top of the vessels from cracking. The goods when dipped into the slip, absorb the water, and the vitriol is deposited upon the surface. They are then inclosed in a dry vessel, and dried, when they are ready for a furnace, to the very highest temperature which can be obtained by artificial means.

The British porcelain is much superior to most others in its power of resisting the action of acids, and a table of its high temperature, has been analysed by Wilson, who found it to consist of

Nitric acid	1000	Lime	0.569
Alumina	1000	Magnesia	0.192
Potash & soda	1000	Potassa	2.001

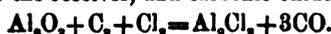
The translucent variety of French porcelain (*porcelaine tendre*) is made of a more fusible paste than ordinary porcelain, that is, of a paste containing a larger quantity of alkali, either in the form of feldspar, or as carbonate or nitrate. The glaze for this porcelain contains oxide of lead to render it more fusible.

The coarser kinds of earthenware are generally glazed with salt (*see p. 273*), but sometimes with a sort of glass containing lead, and occasionally colored with oxides of iron, &c. Pans glazed with lead are somewhat dangerous for culinary purposes.

SESQUICHLORIDE OF ALUMINUM, Al_2Cl_3 .

§ 214. *Preparation*.—When alumina is dissolved in hydrochloric acid, a solution of the sesquichloride is obtained, which, when evaporated *in vacuo*, yields crystals of the formula $Al_2Cl_3 + 12Aq$.

In order to prepare the anhydrous salt, recourse is had to a method often employed in preparing chlorides from oxides, which consists in passing dry chlorine gas over a mixture of the oxide with charcoal, at a red heat. A quantity of perfectly dry alumina is mixed with lampblack and a little oil, to a thick paste, which is moulded into small pellets; these are strongly heated in a closed crucible, then introduced into a porcelain tube or retort, connected at one end with an apparatus for evolving dry chlorine, and at the other with an adapter passing into a flask surrounded with cold water; the tube or retort having been raised to a high temperature, a stream of chlorine is passed, when the sesquichloride of aluminum sublimes into the receiver, and carbonic oxide escapes:—



Properties.—Anhydrous sesquichloride of aluminum is a white, volatile crystalline solid which fumes in contact with air. When thrown into water, it combines with it energetically, with a hissing sound; the solution of sesquichloride of aluminum is decomposed like that of chloride of magnesium when evaporated to dryness; water suffers decomposition, hydrochloric acid passes off, and alumina is left:—



The crystallized hydrate is decomposed in the same manner by heat. It is very deliquescent, and soluble in water and alcohol. Sesquichloride of aluminum is capable of combining with ammoniacal gas.

The *Sesquifluoride of Aluminum*, associated with fluoride of sodium, occurs in nature as the mineral *kryolite*.

When *aluminum* is heated in the vapor of *sulphur*, combination takes place, and a dark gray mass is formed, which assumes a feeble metallic lustre when burnished. When exposed to air, it absorbs moisture, and evolves hydrosulphuric acid. Water resolves it into hydrosulphuric acid and alumina.

No compound of these elements has yet been prepared in the moist way; when an alkaline sulphide is added to a solution of alumina, the latter is precipitated as hydrate, with evolution of sulphuretted hydrogen; thus:—



GLUCINUM (BERYLLIUM).

Sym. Gl (*or* Be). *Eq.* 6.9.

§ 215. This metal is of comparatively rare occurrence in nature, where it exists generally in combination with silicic acid.

The *emerald* is a double silicate of alumina and glucina, colored with sesqui-

oxide of chromium. Its composition may be expressed by the formula $Gl_2O_3 \cdot SiO_2 \cdot Al_2O_3 \cdot SiO_2$.

The *beryl* is a pale green variety of emerald.

Euclase is another mineral containing glucinum; its formula is $2Gl_2O_3 \cdot SiO_2 \cdot 2Al_2O_3 \cdot SiO_2$.

Chrysoberyl has the composition $Al_2O_3 \cdot Gl_2O_3$.

Glucinum may be prepared by decomposing the sesquichloride with potassium, in exactly the same way as aluminum was obtained. Glucinum is very similar to aluminum; it is not oxidized by dry air, and does not decompose water at the ordinary temperature. When heated in air or oxygen, it is converted into glucina (Gl_2O_3).

This metal decomposes water in presence of acids or alkalis.

Only one oxide of glucinum is known.

GLUCINA, Gl_2O_3 .

Preparation.—This oxide is generally prepared from the mineral termed *emerald of Limoges*, which contains silicates of alumina and glucina, together with lime and sesquioxide of iron.

The mineral, in a state of fine powder, is mixed with about three times its weight of carbonate of potassa and fused in a platinum crucible; the fused mass is digested with dilute sulphuric acid, which leaves a quantity of silica undissolved; the filtered solution is evaporated to a small bulk, and allowed to cool, when crystals of alum are deposited; the liquor separated from the crystals is now mixed with excess of ammonia, which precipitates the sesquioxide of iron and the glucina, together with a little alumina; this precipitate is digested with a saturated solution of carbonate of ammonia, which dissolves only the glucina, and deposits the carbonate of this base on ebullition; the precipitated carbonate is washed, dried, and ignited, when pure glucina is left.

Properties.—Glucina much resembles alumina, being white, infusible, and insoluble in water. Unlike that base, however, it absorbs carbonic acid when exposed to air, and expels ammonia from its salts. Glucina is soluble in acids; the salts thus produced have a sweet astringent taste (hence its name, from γλυκύς); they are acid to test-papers. It is also soluble in solutions of potassa and soda, and is reprecipitated when these solutions are diluted with water and boiled.

Glucina is considered by some chemists as a protoxide, but its analogy with alumina favors the view which we have taken above, that it is a sesquioxide.

Glucina is precipitated from its solutions in the form of hydrate.

The *Neutral Sulphate of Glucina* crystallizes in octahedra of the formula $(Gl_2O_3, SO_4) \cdot 12Aq$. It is very soluble in water.

Other sulphates of glucina exist, but it does not form an alum.

A base *Chloride of Glucina*, $(Gl_2O_3, Cl_2) \cdot 5Aq$, is obtained by precipitation; it is soluble in alkaline carbonates.

Sesquichloride of Glucina, Gl_2Cl_3 , may be prepared in the same way as the corresponding aluminum compound, which it much resembles.

Sesquichloride of Glucina, Gl_2Cl_3 , may be obtained by the direct combination of glucinum with chlorine; it is precipitated as a white gelatinous hydrate, on adding a hydrosulphate of an alkaline sulphate to a solution of glucinum.

The compounds of glucinum have as yet no practical application.

Salts of Glucina.—Potassa, soda, and their carbonates produce, in solution of glucina, white precipitates similar to those

of aluminum and sulphate of ammonium also give a gelatinous precipitate, and soda in excess dissolves it in solution of ammonia, and reprecipitated by boiling.

Phosphate of soda precipitates phosphate of glucina.

When a hot solution of *fluoride of potassium* is added to a hot solution of glucina until a precipitate begins to appear, and the solution then cooled, a crystalline precipitate of a double fluoride is produced.

Fixed organic matters interfere with the precipitation of glucina. Glucina does not yield a blue compound with *nitrate of cobalt* before the blowpipe.

THORINUM OR THORIUM.

Sym. Th. Eq. 59.6.

§ 216. This is a very rare metal, found in the minerals *thorite* and *pyrochlorite*. The former contains about 57 per cent. of thorina. The metal itself may be prepared by the same process as aluminum, which it resembles in most of its properties.

It is not easily dissolved by acids, with the exception of hydrofluoric acid; alkalis are said to have no action upon it.

We are acquainted with only one oxide of thorium.

OXIDE OF THORINUM, THORINA, ThO.

Preparation.—This oxide is prepared from thorite, in which it is associated with silica, lime, magnesia, and the oxides of iron, manganese, uranium, lead, and tin. The mineral is boiled with hydrochloric acid, the solution evaporated to dryness, the residue extracted with water, the lead and tin precipitated by sulphuretted hydrogen, and the solution mixed with excess of ammonia, which throws down the thorina, together with the oxides of iron and uranium; the precipitate is dissolved in sulphuric acid, and the solution rapidly boiled down, when sulphate of thorina, being sparingly soluble in hot water, is precipitated; this is collected on a filter, washed with boiling water, and ignited, when pure thorina is obtained as a white powder.

Properties.—This earth is remarkable for its great density (sp. gr. 9.4). It combines with water, forming a hydrate (ThO.HO), which is insoluble in the alkalis, soluble in the acids and in alkaline carbonates. After ignition, however, thorina is soluble only in sulphuric acid.

REACTIONS OF THORINA.—*Potassa*, *soda*, *ammonia*, and *sulphide of ammonium* produce, in solutions of thorina, gelatinous precipitates, insoluble in excess. The *carbonates of potassa* and of *ammonia* produce a precipitate soluble in excess.

Phosphate of soda precipitates phosphate of thorina.

Soluble salts of thorina are decomposed at a red heat.

Solutions of some of these, *e. g.* the sulphate, yield precipitates upon boiling, which redissolve very slowly as the solution cools. This peculiar reaction does not take place when the solution contains any base capable of forming a double-salt with thorina.

YTTORIUM, ERBIUM, AND TERBIUM.

Sym. Y. Sym. E. Sym. Tb.

§ 217. These metals are exceedingly rare, and possess no practical interest. They are found in the minerals *gadolinite*, *orthite*, and *ytrotantalite*.

Yttrium is obtained by decomposing its chloride with potassium; it is very similar to aluminum.

The oxides of these metals, viz. *yttria* (YO), *erbia* (EO), and *terbia* (TbO) are obtained together from the mineral gadolinite.

By digesting the mixed precipitate in very dilute sulphuric acid, the yttria is dissolved, and may be reprecipitated from the solution by potassa. The residue of erbia and terbia is dissolved in nitric acid, and the solution saturated with sulphate of potassa, which yields a sparingly soluble double-salt with the sulphate of erbia. The solution yields terbia upon addition of potassa.

Pure Yttria is a white powder of great density; it dissolves more easily in dilute than in concentrated acids. The *hydrate*, obtained by precipitation, resembles hydrate of alumina.

The solutions of salts of yttria are sweet and astringent; they have an acid reaction.—*Nitrate of Yttria* is white, crystallizable, and deliquescent.—The *sulphate* forms colorless crystals, which are sparingly soluble.—*Chloride of Yttrium* is volatile, crystalline, and deliquescent.

Erbia has a dark yellow color, which it loses when ignited in a current of hydrogen, and regains when gently heated in air. It dissolves in acids, forming colorless salts.

The *sulphate* is crystallizable, and does not effloresce on exposure to air at 176° F. (80° C.).—*Nitrate of Erbium* is not deliquescent; its solution is colorless, even when concentrated.

The *Salts of Terbia* acquire a reddish color upon desiccation.—The *sulphate* is efflorescent at 122° F. (50° C.)

REACTIONS OF YTTRIA, ERBIA, AND TERBIA.—*Potassa, soda, ammonia,* and *sulphide of ammonium*, yield bulky precipitates of the hydrates, insoluble in excess.

Alkaline carbonates; a white precipitate, soluble, though with difficulty, in a large excess.

Phosphate of Soda; a white precipitate, soluble in *hydrochloric acid*, reprecipitated by boiling.

CERIUM, LANTHANUM, DIDYMIUM.

Sym. Ce. Eq. 47. Sym. La. Eq. 47. Sym. D. Eq. 50.

§ 218. *Cerite* is the chief mineral from which these metals are extracted; they exist in it as silicates. They are also contained in gadolinite, orthite, and *yttrite*. Cerium forms two basic oxides, the *oxide* (CeO) and *sesquioxide* (Ce_2O_3).

In order to extract the oxides of cerium, lanthanum, and didymium, the powdered ore is ignited and extracted with *aque regia*; the solution is evaporated to dryness, and the residue treated with dilute hydrochloric acid, which leaves the siliceous undissolved; the filtered liquid is precipitated by ammonia, and the precipitate boiled with an excess of nitric acid which dissolves the sesquioxide of cerium, and leaves the other oxides in the form of azitates; this residue is ignited, and the azides thus obtained are dissolved in concentrated nitric acid; the solution is evaporated to dryness, and the residue ignited when the oxides are left in a very finely divided state. By boiling these with a large quantity of very dilute hydrochloric acid, the oxide of lanthanum is then dissolved, and may be precipitated as phosphate of cerium, lanthanum, and didymium. To separate the didymium and cerium, the residue of the above is treated with anærochloric acid, which dissolves the oxide of didymium, and leaves sesquioxide of cerium.

Cerium, Lanthanum, and Didymium are obtained by reducing their chlorides with potassium; they form gray powders, which become lustrous when burnished; they are very infusible, and non-volatile. These metals oxidize rapidly when exposed to air; they readily decompose water at the boiling-point.

Oxide of Cerium (CeO) is obtained by heating the carbonate in a current of hydrogen. The *hydrate*, obtained by precipitation, is white at first, and becomes yellow when exposed to air, or when treated with chlorine (oxide of lanthanum is not turned yellow by chlorine).

The *Salts of Oxide of Cerium* are colorless, and have an acid reaction. The *nitrate* is soluble and crystallizable.—The *sulphate* crystallizes in hydrated prisms; it forms a nearly insoluble *double salt with sulphate of potassa*.—The *carbonate* is insoluble in water.

Sesquioxide of Cerium (Ce_2O_3) is obtained by heating the metal in air or oxygen. It has a yellow color, which is darkened by ignition. The sesquioxide is slowly acted upon by hydrochloric acid, which forms chloride of cerium, with evolution of chlorine. Sulphuric acid (conc.) dissolves it easily with the aid of heat.

The *hydrated sesquioxide* forms a yellow gelatinous precipitate.—The *neutral sulphate* forms a yellow *double salt with sulphate of potassa*, which is sparingly soluble in water.

Chloride of Cerium (CeCl) is white; soluble in water and alcohol; its solution in the latter burns with a green flame.—*Sulphide of Cerium* has a yellow or red color, and is easily dissolved by acids.

Only one *Oxide of Lanthanum* (LaO) is known; it is a white powder, soluble in acids, and in ammoniacal salts, from which it expels the ammonia. The *hydrate*, obtained by precipitation, rapidly absorbs carbonic acid from the air. The *salts of oxide of lanthanum* have a sweet astringent taste. The *nitrate* crystallizes in deliquescent prisms.—*Sulphate of lanthanum* forms six-sided crystals of the formula $\text{LaO}\cdot\text{SO}_3 + 3\text{Aq}$, which are soluble in 6 parts of cold water and in 120 of boiling water. A solution of this salt, saturated at a low temperature, deposits the greater part of the sulphate when heated to ebullition.—*Carbonate of lanthanum* has been found native. The *chloride* is very soluble.

The *Oxide of Didymium* (DO) has a dark color. The *hydrate* has a violet color, and absorbs carbonic acid from the air. It dissolves readily in acids, and expels ammonia from its salts, but is a weaker base than oxide of lanthanum. Its *salts* have a pink or violet color. The *nitrate* crystallizes with difficulty, and is deliquescent; its solution has a deep red color. The *sulphate* forms red crystals, which are more soluble in cold than in hot water. It yields a *double-salt* with sulphate of potassa.

REACTIONS OF (OXIDES OF) CERIUM, LANTHANUM, AND DIDYMIUM.—*Potassa, soda, ammonia, and sulphide of ammonium*; a white hydrate, insoluble in excess.—The *alkaline carbonates*; precipitate, very sparingly soluble in excess.—*Phosphate of soda*; a white precipitate.—*Sulphate of potassa*; a crystalline precipitate. With a *borax-bead*, in the outer blowpipe-flame, a reddish-yellow, which fades on cooling, and vanishes in the inner flame.

The reactions of lanthanum closely resemble those of cerium, but the former metal is not precipitated from its solutions by *sulphate of potassa*.

The solutions of didymium, as stated above, have a violet color. *Sulphide of ammonium* precipitates them with difficulty in the cold. *Sulphate of potassa* gives an amethyst-colored double-salt. With a bead of *phosphorus-salt*, in the inner flame, a red glass with a shade of violet.

ZIRCONIUM.

Sym. Zr. Eq. 22.4.

§ 219. This rare metal exists in the minerals *zircon* and *hyacinth*, which are chiefly composed of *silicate of zirconia* ($Zr_2O_3 \cdot SiO_2$).

The metal, which is prepared by the action of potassium upon the double fluoride of zirconium and potassium, is a black powder, capable of assuming a metallic lustre. When heated in air, it is converted into zirconia.

Alkalies, their carbonates, and even borax, are capable of oxidizing this metal, but it is not attacked to any extent by acids, except hydrofluoric.

The only oxide of this metal, *zirconia* (Zr_2O_3), is, in many respects, similar to alumina.

In order to extract this base from hyacinth, the mineral is fused with hydrate of potassa; the fused mass is decomposed with hydrochloric acid, and the silica separated in the usual manner; the solution freed from silica is treated exactly as in the extraction of cerium from cerite (see p. 324).

Zirconia is a white powder, slightly soluble in carbonate of ammonia and in the alkaline bicarbonates. After ignition, it can be dissolved only by sulphuric acid. A *hydrate* of zirconia has been obtained. The *neutral salts* of zirconia redden litmus. The *nitrate* does not crystallize, and is very soluble. The *neutral sulphate* is crystalline and soluble; other sulphates exist. The *carbonate* is insoluble. Anhydrous *sesquichloride of zirconium* is not volatile; the *hydrated chloride* crystallizes.

REACTIONS OF ZIRCONIA.—*Potassa, soda, ammonia, and sulphide of ammonium*; a white precipitate, insoluble in excess. *Alkaline carbonates*; precipitate, soluble in large excess. *Phosphate of soda*; white precipitate. *Sulphate of potassa*; a double sulphate, sparingly soluble in water and acids, when precipitated from hot solutions.

CHROMIUM.

Sym. Cr. Eq. 26.7. Sp. Gr. 5.9.

§ 220. Chromium is moderately abundant in nature, but not in the free state.

It is found in *chromo-iron* (a compound of the oxides of chromium and iron), and as *chromate of lead*.

The *ruby* also contains chromic acid, to which its color is due; this gem contains 82.5 per cent. alumina, 8.9 per cent. magnesia, and 6.2 per cent. chromic acid.

As already stated, the green color of the *emerald* is due to sesquioxide of chromium.

Preparation.—Chromium may be prepared by exposing to a very high temperature, in a crucible lined with charcoal, an intimate mixture of sesquioxide of chromium and charcoal: the spongy mass thus obtained is powdered in an iron mortar and mixed with a little more sesquioxide of chromium (to oxidize as much of the carbon as possible): the mixture is again exposed to a very high temperature in a porcelain crucible, when a coherent mass of metal is obtained. The chromium thus prepared always contains more or less carbon.

It may be obtained in a purer state by the action of potassium upon sesquichloride of chromium.

Properties.—The metal obtained by the first process forms a grayish, hard, brittle mass, which assumes the metallic lustre when burnished. Chromium is magnetic only at very low temperatures; and is very infusible. It is not oxidized in dry air, except at a red heat, when it is converted into sesquioxide. This metal does not decompose water, even at the boiling-point. It is attacked with considerable difficulty by acids, but, when heated with hydrated alkalis, is converted into chromic acid with evolution of hydrogen. Chlorates and nitrates are also capable of converting chromium into chromic acid.

When the metal is prepared by reducing sesquichloride of chromium with potassium, it forms a gray powder, which is oxidized far more readily than the preceding, and dissolves much more easily in acids and alkalis.¹

The metal itself has hitherto received no practical application.

CHROMIUM AND OXYGEN.*

Oxide (protoxide) of chromium	CrO.
Sesquioxide of chromium	Cr ₂ O ₃ .
Chromic acid	CrO ₃ .
Perchromic acid	Cr ₂ O ₇ .

OXIDE OF CHROMIUM, CrO.

§ 221. This oxide possesses little practical interest, and has never been obtained in a pure state. It is precipitated as a brown hydrate, when (proto-) chloride of chromium is decomposed by potassa; almost as soon as it is liberated, however, it decomposes water, seizing its oxygen and becoming converted into a compound of oxide and sesquioxide of chromium. It is a feeble base; its salts are little known.²

SESQUIOXIDE OF CHROMIUM, CHROME, CHROMIC OXIDE.

Cr₂O₃. Eq. 77.4.

The sesquioxide is found in nature in the anhydrous state, and in combination with water; the chief source of sesquioxide of chromium is the *chrome-iron ore*, which may be represented by the formula FeO.Cr₂O₃. It is sometimes met with in octohedral crystals, being isomorphous with spinelle (MgO.Al₂O₃), and the magnetic-iron ore (FeO.Fe₂O₃). Chrome-iron is found chiefly in Sweden, in Russia, and in the United States. (For the analysis of chrome-iron ore, see Quantitative Analysis, Special Methods.)

Preparation.—Sesquioxide of chromium cannot be prepared directly from chrome-iron ore, but is always first converted into chromic acid.

Since the oxide is extensively employed for coloring porcelain and glass, some attention has been paid to its preparation, and several different processes have been proposed, which furnish products varying much in tint.

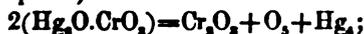
I. When solutions of subnitrate of mercury (Hg₂O.NO₂) and of chromate of potassa (KO.CrO₃) are mixed, a red precipitate of subchromate of mercury

¹ According to Berzelius, this difference is due to an allotropic state of the metal.

² In the list of oxides, we have refrained from mentioning those which are merely *compounds*, and not *independent* oxides. This will be always done, unless the intermediate oxides are of considerable importance.

³ A double sulphate of oxide of chromium and potassa (CrO.SO₃.KO.SO₃+6Aq), isomorphous with the double sulphate of iron and potassa, is obtained by addition of alcohol to a mixture of solutions of sulphate of potassa and chloride of chromium. Its solution has a blue color, and becomes rapidly green when exposed to the air.

($\text{Hg}_2\text{O} \cdot \text{CrO}_3$) is obtained; if this precipitate be washed, dried, and ignited, mercury and oxygen are expelled, and chromic oxide left:—



the oxide thus obtained is a powder of a fine green color.

II. If bichromate of potassa ($\text{KO} \cdot 2\text{CrO}_3$) be mixed with an equal weight of sulphur, and the mixture calcined, a residuum will be obtained, which consists of sulphate of potassa and sesquioxide of chromium:—



the sulphate of potassa is extracted with water.

III. By calcining a mixture of the bichromate with charcoal, and washing the residuum with water:—



IV. A very fine product may also be obtained by employing starch in place of charcoal.

V. The precipitated hydrate of sesquioxide of chromium may be rendered anhydrous by a moderate heat.

VI. When chromate of potassa is heated to redness in a current of chlorine, green crystalline plates of the sesquioxide are obtained:—



VII. Chromic oxide may also be obtained in very hard, dense, dark-green octohedra (isomorphous with corundum) by passing the vapor of chlorochromic acid (CrO_2Cl) through a red-hot porcelain tube:—



VIII. By igniting a mixture of 3 parts of chromate of potassa, and 2 parts of chloride of ammonium, when sesquioxide of chromium and chloride of potassium are left; water and nitrogen being evolved.

Properties.—Anhydrous sesquioxide of chromium is a bluish-green powder, unaltered by exposure to air. When heated, its color changes, incandescence is observed, and the properties of the sesquioxide are found considerably modified; it becomes almost insoluble in acids and alkalis, and is hence said to be converted into the insoluble modification. If it has not been strongly ignited, however, sesquioxide of chromium is soluble, though not very easily, in the stronger acids, and in solutions of potassa and soda; from the latter it is reprecipitated by boiling.

When fused with oxidizing agents (hydrated alkalis, nitrates, chlorates) in the presence of alkalis, sesquioxide of chromium is converted into chromic acid.

The sesquioxide cannot be reduced by hydrogen, and is acted on by carbon only at a very high temperature.

HYDRATE OF SESQUIOXIDE OF CHROMIUM, $\text{Cr}_2\text{O}_3 \cdot 10\text{HO}$.¹

Preparation.—A pretty strong solution of bichromate of potassa is mixed with a moderate quantity of hydrochloric acid, introduced into a deep vessel, and a stream of sulphurous acid (prepared by the action of charcoal on oil of vitriol) passed, until the red color has changed to a pure green, and the odor of sulphurous acid does not disappear even on standing:—



the solution containing sulphate of sesquioxide of chromium is now mixed with a slight excess of ammonia, and heated, when the whole of the sesquioxide of chromium is precipitated as a basic hydrate, which, when dried at the ordinary temperature, has the formula given above:—



¹ From a source it that contains 2HO.

Properties.—This hydrate is entirely deprived of its water by exposure to a temperature of 392° F. (200° C.); it dissolves with facility in solutions of potassa and soda, forming fine green solutions, which deposit after a time a hydrate of the formula $\text{Cr}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$, which is insoluble in the alkalies; probably it is in this form that the whole of the sesquioxide is precipitated (as mentioned before) on boiling the alkaline solutions.

Hydrated sesquioxide of chromium dissolves to a slight extent in solution of ammonia, forming a pink solution, which deposits all the chromium when boiled.¹

The soluble salts of sesquioxide of chromium have an acid reaction.

NITRATE OF SESQUIOXIDE OF CHROMIUM, $\text{Cr}_2\text{O}_3 \cdot 3\text{NO}_3$.—This unimportant salt may be prepared by dissolving the hydrated sesquioxide in nitric acid, and evaporating; it has a green color, and is easily decomposed by heat, yielding a brown substance, which is said to be $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$. This nitrate is very soluble in water.

SULPHATE OF SESQUIOXIDE OF CHROMIUM, $\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3$.

This salt is known in three modifications, exhibiting a difference in their properties which justifies us in describing them separately.

Violet Salt, $\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3 + 15\text{Aq}$.—This salt is obtained when 8 parts of hydrated sesquioxide of chromium, which has been dried at 212° F., are digested for some weeks with 8 or 10 parts of concentrated sulphuric acid; in this way a bluish-green crystalline mass is obtained, which is purified by dissolving in water and adding alcohol, which throws down a violet crystalline precipitate; this is redissolved in weak alcohol, and allowed to evaporate spontaneously, when octohedral crystals are deposited, which have a violet color, and the composition given above. This salt is very soluble in water; the solution is acid.

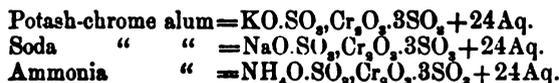
Green Salt, $\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3 + 15\text{Aq}$.—The green sulphate is formed when hydrated sesquioxide of chromium is dissolved in concentrated sulphuric acid with the aid of a gentle heat. It may also be obtained by rapidly evaporating a solution of the violet salt.

This green salt differs from the violet modification by its solubility in alcohol. When heated it undergoes the aqueous fusion, and loses 10 eqs. of water at 212° F. (100° C.) It has been stated that the solution of this salt is not entirely decomposed by solution of baryta in the cold, and therein differs from the violet sulphate.

Red Salt, $\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3$.—This salt is prepared by heating either of the above modifications with an excess of concentrated sulphuric acid to about 392° F. (200° C.), and evaporating to expel excess of acid. This variety of sulphate of sesquioxide of chromium is characterized by its insolubility in water and acids.

Basic sulphates of sesquioxide of chromium are known.

Sesquioxide of chromium, like alumina, forms a series of *alums* perfectly analogous to those of the latter base.



POTASH-CHROME ALUM.

Preparation.—This alum is very conveniently prepared by mixing three measures of a saturated solution of bichromate of potassa with one measure of

¹ Some of the violet salts of chromium when treated with alkalies, yield a violet precipitate which dissolves completely in ammonia. Other hydrates of sesquioxide of chromium, containing 8, 4, and 8 eqs. of water, are said to have been obtained.

concentrated sulphuric acid, and saturating with sulphurous acid; after a time crystals of chrome alum are deposited:—



Another method consists in mixing a concentrated solution of the bichromate with sulphuric acid, allowing the liquid to cool, and gradually adding alcohol (assisting the reaction, if necessary, with a gentle heat) till the red color of the solution has changed to violet; on standing the chrome-alum is deposited. Sugar is sometimes employed instead of alcohol as a reducing agent.

Properties.—The chrome-alum thus obtained is deposited in octohedral crystals, of a purple-red color, which appear ruby-red by transmitted light. It is very soluble in water, and when heated, it undergoes the aqueous fusion, and at 392° F. (200° C.), loses 22 eqs. of water, and is converted into a green modification. At about 662° F. (350° C.), it becomes anhydrous, and ultimately yields a lilac powder, which is soluble only in oil of vitriol. Chrome-alum is very soluble in water, and gives an acid solution of a dark violet color. If this solution be allowed to evaporate spontaneously, it deposits the ordinary crystals of chrome-alum, but if evaporated at about 176° F. (80° C.), it assumes a green color, and does not yield any crystals, since it is then either decomposed or converted into the alum corresponding to the green sulphate of sesquioxide of chromium, which does not crystallize, but is left as a green mass on evaporation; the solution, however, resumes its normal condition after long standing. Chrome-alum is insoluble in alcohol. It is employed in dyeing, and is hence, to some extent, an article of commerce.

The action of ammonia upon a solution of chrome-alum tends to demonstrate the existence of different modifications of the hydrates of sesquioxide of chromium, corresponding to the different varieties of the sulphate. When solution of chrome-alum is added, drop by drop, to an excess of ammonia, the precipitated hydrate has a green color, and yields a violet solution with sulphuric acid.

If the chrome-alum be decomposed by a quantity of ammonia insufficient to redissolve any portion of the hydrate, the latter will have a violet color, and will dissolve in sulphuric acid to form a red solution.

A *basic carbonate of sesquioxide of chromium* is obtained, as a green precipitate, when a solution of sesquioxide of chromium is decomposed by an alkaline carbonate. Its formula is $4\text{Cr}_2\text{O}_3 \cdot \text{CO}_2 + 3\text{Aq}$; it is soluble in the alkaline carbonates with the aid of heat.

PROTOSSESQUIOXIDE OF CHROMIUM, $\text{Cr}_2\text{O}_3 = \text{CrO} \cdot \text{Cr}_2\text{O}_3$.—This oxide is formed (as we have seen already) when a solution of potassa is added to a salt of (prot-) oxide of chromium, water being decomposed:—



This oxide is thus obtained as a brown hydrate, which is converted into sesquioxide when heated in air.

From the foregoing description of the properties of sesquioxide of chromium and its compounds it will be seen that we are justified in placing it in juxtaposition with alumina and the other earths.

CHROMIC ACID (CrO_3).

§ 200. It has already been stated that this acid occurs in nature in combination with oxide of lead.

It is prepared by adding to one measure of a saturated solution of bichromate of potassa, or about 150° F. part of one measure and a half of concentrated sulphuric acid, and allowing the solution to cool, when crystals of chrome alum are deposited, and the excess of potassa remains in solution. The crystals are drained and separated with a platinum knife, drained in a funnel supported with a low plug of asbestos, and dried at the ordinary tempera-

ture upon a porous tile; they must not be heated, or brought in contact with paper, lest they suffer decomposition. In order to free them from adhering sulphuric acid, they may be dissolved in a very little water, the solution digested with chromate of baryta, which precipitates the sulphuric acid, the clear liquid decanted, and evaporated *in vacuo* over oil of vitriol.

Properties.—Chromic acid crystallizes in fine red needles, which are deliquescent, and very soluble in water. They stain the skin yellow. When heated, the crystals assume a very dark color, and are afterwards decomposed into sesquioxide of chromium and oxygen, often with incandescence.

The aqueous solution of chromic acid has an orange-red color; when exposed to sunlight, it evolves oxygen, and deposits the chromate of sesquioxide of chromium. Chromic acid is dissolved by weak alcohol, but the solution soon decomposes, from the action of the chromic acid on the alcohol.

When absolute alcohol is poured upon crystals of chromic acid, the former is rapidly oxidized, often with sufficient energy to give rise to combustion, the chromic acid being reduced to sesquioxide of chromium.

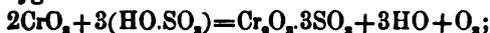
Chromic acid, indeed, is one of the most powerful oxidizing agents with which we are acquainted. The deoxidizing action of sulphurous acid upon chromic acid has been already mentioned.

When chromic acid is heated with hydrochloric acid, chlorine is evolved, and sesquichloride of chromium formed:—



Sugar, and many other organic substances, are also capable of reducing this acid.

When chromic acid (or bichromate of potassa) is heated with concentrated sulphuric acid, oxygen is evolved:—



A mixture of 5 parts of bichromate of potassa and 4 of concentrated sulphuric acid has been recommended for the preparation of oxygen in the laboratory.

If crystals of chromic acid are placed in a bulb-tube, and gently heated in a current of dry ammonia, vivid incandescence is observed, and the chromic acid is reduced:—



Chromic acid is extensively used as an oxidizing agent in experiments upon organic substances.

Compounds of chromic acid with *sulphuric acid* have been obtained.¹

Chromic acid is monobasic, and forms an extensive series of salts, which have the same crystalline form as the corresponding sulphates, chromic acid being isomorphous with sulphuric acid. The general formula of the neutral chromates may be written MO.CrO_3 . The neutral chromates of the alkalis have a fine yellow color; the acid chromates are orange-red.

CHROMATE OF POTASSA, KO.CrO_3 .

This salt is prepared by adding carbonate of potassa to a solution of the bichromate, until it assumes a fine yellow color, evaporating and crystallizing.

Properties.—The chromate is thus obtained in bright yellow anhydrous crystals, of the same form as those of sulphate of potassa. They are unaltered in air.

When heated, the salt changes color to red, fuses at a red heat, but does not suffer decomposition; it assumes its original yellow color on cooling.

This chromate is easily soluble in cold water, and much more so in hot; the

¹ Schrötter has recently obtained a compound of anhydrous sulphuric and chromic acids.

solution has a bright yellow color, even though it contain very little chromate; it has a bitter taste, and an alkaline reaction.

When solution of chromate of potassa is kept in bottles of ordinary English glass, these are attacked, and a yellow substance (probably chromate of lead) deposited upon the interior surface.

Chromate of potassa does not dissolve in alcohol; it is a poisonous salt.

When the yellow solution of chromate of potassa is mixed with an acid, its color changes to red, from production of the bichromate.

If sulphuretted hydrogen be added to an aqueous solution of the chromate, sesquioxide of chromium and sulphur are precipitated, while sulphide of potassium is found in solution:—



BICHROMATE OF POTASSA, KO.2CrO_3 .

Preparation.—Chrome-iron ore is reduced to powder, and fused in a reverberatory furnace with half its weight of nitre, with continual stirring; in this way the chromium is converted into chromate of potassa, and the silica and alumina contained in the ore are rendered soluble in water; the mass is extracted with boiling water, and the solution mixed with a slight excess of acid (sulphuric, nitric, or acetic), which precipitates the alumina and silica, and converts the chromate into bichromate, which may be crystallized from the solution, and purified by recrystallization.

Bichromate of potassa may also be prepared by heating a mixture of chrome-iron ore and chalk in an oxidizing flame. The mass, containing chromate of lime, is suspended in water, and converted into bichromate by addition of sulphuric acid. The resulting bichromate of lime is decomposed with carbonate of potassa.¹

Properties.—The bichromate forms beautiful red tabular crystals, derived from an oblique rhombic prism; they are not changed by exposure to air, and are anhydrous.

When heated, this salt fuses easily, without alteration, but at a high temperature is decomposed into chromate of potassa, crystalline sesquioxide of chromium, and oxygen:—



Bichromate of potassa is less soluble than the chromate, one part of the former salt requiring ten parts of cold water. It is more soluble in hot water; the solution has a fine red color and an acid reaction. This salt is insoluble in alcohol.

The bichromate is a more powerful oxidizing agent than the chromate. Most reducing agents decompose it, either at the ordinary, or at a slightly elevated temperature.

Uses of Chromate of Potassa.—The chromate and bichromate of potassa are somewhat extensively used in dyeing, and in the manufacture of colors. The bichromate is also employed in bleaching sperm-oil, for which purpose the latter is heated with a mixture of bichromate of potassa and sulphuric acid, which oxidizes the coloring matter; the sulphate of sesquioxide of chromium thus produced is afterwards recovered into bichromate.

Chromate and bichromate of potassa are employed as reagents. A mixture of bichromate of potassa and sulphuric acid is frequently made use of in the laboratory as an oxidizing agent. These salts are also employed for the preservation of wood.

¹ Nöblin has proposed to prepare the bichromate of potassa by fusing chrome-ore, mixed with sulphate of potassa, and nitre, in a reverberatory furnace through which a current of steam is passed. He also recommends the fusion of the ore with potassium sulphate and nitre.

Bichromate of potassa forms a *double salt* with *sulphate of potassa*, which may be obtained in bright crystals of the formula $\text{KO} \cdot 2\text{CrO}_3 \cdot \text{KO} \cdot \text{SO}_4$. It is very soluble, and may be fused without decomposition.

Terchromate of Potassa, $\text{KO} \cdot 3\text{CrO}_3$, is obtained in anhydrous red crystals by decomposing bichromate of potassa with excess of nitric acid.

Bichromate of Chloride of Potassium, *Chlorochromate of Potassa*, $\text{KCl} \cdot 2\text{CrO}_3$.—This salt is deposited in fine red prisms, from a mixture of bichromate of potassa and hydrochloric acid, which has been boiled until chlorine begins to escape.

Though permanent in dilute hydrochloric acid, it is decomposed by water into hydrochloric acid and bichromate of potassa :—



this decomposition would lead us to regard the compound as bichromate of potassa, in which one equivalent of chromic acid has been replaced by chlorochromic acid (CrO_2Cl ; p. 334).

When treated with oil of vitriol, it evolves chlorochromic acid.

The *Chromate of Soda* is very soluble in water and deliquescent; its crystals have the same form as those of sulphate of soda ($\text{NaO} \cdot \text{SO}_3 + 10\text{Aq}$), and a corresponding formula, $\text{NaO} \cdot \text{CrO}_3 + 10\text{Aq}$.

The *Bichromate of Ammonia*, recently examined by Richmond and John Abel, has the formula, $\text{NH}_4\text{O} \cdot 2\text{CrO}_3$, and is decomposed by heat in a peculiar manner, leaving sesquioxide of chromium :—



Several *chromates of sesquioxide of chromium* appear to exist.

The residue left on gently igniting the nitrate of sesquioxide of chromium has the formula $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$, and is viewed by some as a binoxide of chromium.

When chromate of potassa is very gradually added to sulphate of sesquioxide of chromium, the *neutral chromate of sesquioxide of chromium*, $\text{Cr}_2\text{O}_3 \cdot 3\text{CrO}_3$, is precipitated. The chromic acid may be removed from this compound by long washing.

On adding chromate of potassa to a solution of chrome-alum, a precipitate is obtained of the formula $3\text{Cr}_2\text{O}_3 \cdot 2\text{CrO}_3 + 2\text{Aq}$.

Lastly, a red-brown, soluble acid salt, of the formula $\text{Cr}_2\text{O}_3 \cdot 4\text{CrO}_3$, is obtained by saturating a solution of chromic acid with hydrated sesquioxide of chromium.

PERCHROMIC ACID, Cr_2O_7 .

When solution of bichromate of potassa is mixed with hydrochloric acid, and a little binoxide of barium added, or when binoxide of hydrogen is added to solution of chromic acid, a fine blue solution is produced, which contains perchromic acid. This acid is very unstable, and has never been obtained in the pure state. Its solution readily loses oxygen, sesquioxide of chromium (not chromic acid) being produced.

Its salts have not yet been prepared.

§ 223. *Nitride of Chromium* (Cr_3N_3) is obtained as a brown powder when sesquichloride of chromium is heated in a current of dry ammonia. When heated in air, this compound burns, and is converted into sesquioxide of chromium, nitrogen being disengaged. It is insoluble in water.

CHLORIDE OF CHROMIUM, PROTOCHLORIDE, CrCl .

This chloride is prepared by passing a current of hydrogen over sesquichloride of chromium heated to redness.

It is a white salt, which is soluble in water; the solution has a blue color, and is very prone to absorb oxygen from the air, being converted into an *oxychloride*,

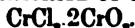
$\text{Cr}_2\text{Cl}_2\text{O}$. The chloride of chromium possesses the same property as the proto-salts of iron, of absorbing the binoxide of nitrogen.

SESQUICHLORIDE OF CHROMIUM, Cr_2Cl_2 .

The anhydrous sesquichloride may be prepared by passing a current of dry chlorine over a mixture of sesquioxide of chromium and charcoal heated to redness; the details of the process are the same as in that for preparing sesquichloride of aluminum; a very high temperature is required. The sesquichloride condenses partly on the upper wall of the tube, and partly in the cool extremity, in fine shining leaflets, of a peach-blossom color. These are unalterable in air, and insoluble in cold water. When boiled with water, they gradually dissolve, yielding a green solution. It is a very peculiar circumstance, that, if a small quantity (a mere trace) of protochloride of chromium be dissolved in the water, the sesquichloride dissolves readily in the liquid, with disengagement of heat, and forms a green solution. A solution of sesquichloride of chromium may be readily prepared by dissolving the hydrated sesquioxide in hydrochloric acid, or by heating bichromate of potassa with hydrochloric acid and a little alcohol; the solution has a fine green color; and if evaporated *in vacuo*, leaves a deliquescent green mass of the formula $\text{Cr}_2\text{Cl}_2 + 9\text{Aq}$, which is considered, by some chemists, as a hydrochlorate of sesquioxide of chromium, $\text{Cr}_2\text{O}_3 \cdot 3\text{HCl} + 6\text{Aq}$.¹ If this green mass be heated, hydrochloric acid is evolved, and the residue contains both sesquioxide and sesquichloride of chromium; when heated in a current of hydrochloric acid gas, the anhydrous sesquichloride is left.

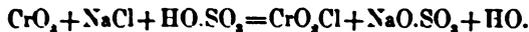
A violet modification of the hydrated sesquichloride of chromium is obtained in solution, when the violet sulphate of the sesquioxide is decomposed by chloride of barium.

CHLOROCHROMIC ACID, BICHROMATE OF PERCHLORIDE OF CHROMIUM.



This substance is more conveniently regarded as a new acid produced by the substitution of 1 eq. Cl for 1 eq. O in chromic acid; its formula will then be CrO_2Cl .

Preparation.—10 parts of common salt are fused with 17 parts of bichromate of potassa in a Hessian crucible; the fused mass is poured out on a clean slab, broken up into small fragments, and introduced into a retort with 30 parts of concentrated sulphuric acid; the retort is connected with a good condensing arrangement, and heat applied gradually by means of a sand-bath, when the substance is easily distilled over. Its production is represented by the following equation:—



Properties.—Chlorochromic acid is a deep brown-red oily liquid, somewhat similar to bromine; its sp. gr. is 1.71. Even at ordinary temperatures this liquid emits dark-brown vapors, and fumes strongly in the air; its odor is very pungent, and recalls that of chlorine. Chlorochromic acid boils at about 250° F. (121° C.), and yields a vapor of sp. gr. 5.55. Water decomposes this acid, yielding chromic and hydrochloric acids:—



therefore, when brought into contact with solutions of the alkalis, it yields chlorides and chromates.

¹ A freshly prepared (green) solution of this compound only loses two-thirds of its chlorine when treated with nitrate of silver; the filtrate, by spontaneous evaporation, deposits green crystals of the formula $\text{Cr}_2\text{O}_3\text{Cl} \cdot 2\text{HCl} + 10\text{Aq}$. By treating a solution of this compound with baryta, precipitating the chloride of barium with alcohol, and evaporating the solution *in vacuo*, a resinous substance is left, having the formula $\text{Cr}_2\text{O}_3\text{Cl} + 3\text{Aq}$.

Chlorochromic acid is a very powerful oxidizing and chlorinating agent; few oxidizable substances can withstand its action.

It is occasionally used to illustrate the nature of illuminating flames; for if hydrogen be passed through a Woulfe's bottle, at the bottom of which a few drops of this liquid are placed, the gas carries up a quantity of the vapor; and if it be then kindled, burns with a brilliant white flame, which deposits a beautiful green film of sesquioxide of chromium upon a porcelain dish depressed into it.

A compound of *chromium with fluorine* is obtained, as a red gas, condensable to a blood-red liquid, when a mixture of a chromate with fluorspar is distilled with concentrated sulphuric acid.

The *Sulphides of Chromium* are imperfectly known.

When a solution of a sulphide is added to one of sesquioxide of chromium, the latter is precipitated as hydrate, with disengagement of sulphuretted hydrogen. If vapor of bisulphide of carbon be passed over sesquioxide of chromium at a red heat, a substance resembling graphite is obtained, having the composition Cr_2S_3 .

It is said that when sulphate of sesquioxide of chromium is heated in a current of hydrogen, a brownish-black pyrophoric *sulphide of chromium*, CrS , is obtained.

A *tersulphide*, CrS_3 , is also said to exist.

URANIUM.

Sym. U. Eq. 60.

§ 224. This metal occurs, though not abundantly, in nature, in the minerals *pitchblende*, in which it exists as black oxide (U_4O_9), associated with silica, oxide of lead, and oxide of iron, *uran-mica*, or *chalcocite*, which contains the oxides of uranium and copper combined with phosphoric acid ($\text{CuO} \cdot 2\text{U}_2\text{O}_3 \cdot \text{PO}_5 \cdot 8\text{Aq}$), and *uranite*, which is a double phosphate of lime and sesquioxide of uranium ($\text{CaO} \cdot 2\text{U}_2\text{O}_3 \cdot \text{PO}_5 \cdot 8\text{Aq}$).

Uranium may be isolated in the same way as magnesium, by heating the (proto-) chloride with potassium, and washing the product with water.

The metal thus obtained is a dark powder, which, when aggregated, forms a lustrous white mass, which is in some degree malleable. It is scarcely altered by exposure to air. When moderately heated, it burns vividly, and is converted into an oxide of a green color. Uranium does not decompose water at the ordinary temperature, but in the presence of acids it dissolves with evolution of hydrogen.

URANIUM AND OXYGEN.

Suboxide	U_2O_3 .
Oxide of protoxide	UO .
Sesquioxide or peroxide	U_2O_5 .

The *suboxide* is little known, and has been obtained by decomposing a subchloride of uranium (U_2Cl_3) with ammonia; it decomposes water, evolving hydrogen, and forming a higher oxide, which is said to be another suboxide, and is still further oxidized on exposure to air.

OXIDE (PROTOXIDE) OF URANIUM, UO .

This oxide was formerly supposed to be the metal. It may be prepared by heating the oxalate of sesquioxide of uranium to redness in a current of hydrogen.

It is thus obtained as a black powder, which takes fire when exposed to air, and is converted into the oxide U_3O_8 .

The *hydrate of (prot-) oxide of uranium* is precipitated in red-brown flocks, where ammonia is added to a salt of this base. The hydrate is soluble in acids.

The *sulphate of (prot-) oxide of uranium*¹ is prepared by decomposing the (proto-) chloride with sulphuric acid. It forms yellow crystals of the formula $UO.SO_3 + 4Aq$. This salt is easily converted by oxidizing agents into the sulphate of sesquioxide; if treated with a large quantity of water, a subsulphate is left.

The *proto-sesquioxide (black oxide)*, U_3O_8 , above referred to, appears to be a combination of (prot-) oxide and sesquioxide of uranium $U_3O_8 = 2UO.U_2O_3$. When heated to redness in the air it absorbs oxygen, and is converted into the green oxide, U_3O_9 , which is probably another proto-sesquioxide of uranium, corresponding to the magnetic oxide of iron. Heated in hydrogen it yields (prot-) oxide of uranium.

SESQUIOXIDE (PEROXIDE) OF URANIUM, U_2O_5 .

This is the most important of the oxides of uranium.

It may be prepared by exposing the nitrate of sesquioxide of uranium, in an oil-bath, to a temperature of 482° F. (250° C.)

The *hydrate*, $U_2O_5.HO$, which occurs native in the form of *uranium-ochre*, is obtained by treating the nitrate with alcohol, evaporating the solution, and extracting the residue with water, which leaves the yellow hydrated sesquioxide. This hydrate loses its water at 572° F. (300° C.), and at a higher temperature, is converted, with evolution of oxygen, into U_2O_5 . Another hydrate, containing 2 eqs. water, is obtained when the result of the preceding operation is dried by mere exposure to air.

Sesquioxide of uranium dissolves in acids forming salts, the solutions of which have a fine yellow color and an acid reaction. These salts present a very anomalous composition, since their general formula is $U_2O_5.RO$ (where RO represents acids generally), whereas the ordinary formula for the neutral salts of sesquioxides is $M_2O_3.3RO$.

Peligt avoids this anomaly by assuming the existence of a radical, *uranyle* = U_2O_5 , of which U_2O_3 is a (prot-) oxide.*

Sesquioxide of uranium occasionally plays the part of an acid, forming combinations with bases which appear to have the general formula $MO.2U_2O_5$, and are, for the most part, insoluble. Sesquioxide of uranium is used to a considerable extent for imparting a yellow color to glass and porcelain.

NITRATE OF SESQUIOXIDE OF URANIUM, $U_2O_5.NO_3$.

This salt generally serves as the source from which the other compounds of uranium are obtained. It is prepared from pitchblende, which has been already mentioned as containing a proto-sesquioxide of uranium, together with silica, oxide of lead, and oxide of iron; it contains moreover, usually, a little copper, arsenic, and sulphur.

In order to prepare the nitrate, pitchblende is reduced to powder and extracted with nitric acid; the solution is evaporated to dryness; on extracting the residue with water, some sulphate of lead and acetate of sesquioxide of iron are left. The residue is saturated with superoxygenated hydrogen, which precipitates the

* The term *uranyle* is used by the author when *proto-oxide of uranium (uranyle)* is mentioned, and *uranyle* is used when the *sesquioxide of uranium* is mentioned and replaced by the *sesquioxide of uranium* or *oxide of uranyle* (or *oxide of uranyle*) (p. 386).

remainder of the lead, arsenic, and copper, and the filtered liquid evaporated to dryness; the residue is treated with water (which leaves a little sesquioxide of iron undissolved), and the solution evaporated to crystallization.¹ In order to purify the crystals thus obtained, they are dissolved in ether, crystallized by spontaneous evaporation, and recrystallized from water.

This salt forms fine yellow crystals, of the formula $U_2O_5 \cdot NO_3 + 6Aq$. When heated, it undergoes the aqueous fusion, loses water, then parts with its acid, and subsequently with more or less oxygen. It is very soluble in water.

Uranate of potassa ($KO \cdot 2U_2O_5$) is obtained as a yellow powder when a salt of sesquioxide of uranium is precipitated with an excess of potassa, or when sesquioxide of uranium is fused with carbonate of potassa. A corresponding compound of soda is obtained in a similar manner.

Sulphate of Sesquioxide of Uranium crystallizes in small prisms, having the formula $U_2O_5 \cdot SO_3 + 3Aq$. When heated to 212° F., they lose 2 eqs. of water, and become anhydrous at 572° F. (300° C.); the anhydrous salt absorbs 8Aq. when exposed to air. According to Ebelmen, a solution of this salt in alcohol, when exposed to the sun's rays, deposits the whole of the uranium as sulphate of the (prot-) oxide. It combines with sulphate of potassa, forming a double-salt (not an *alum*) of the formula $KO \cdot SO_3 \cdot U_2O_5 \cdot SO_3 + 2Aq$.

CHLORIDE (OR PROTOCHLORIDE) OF URANIUM, UCl .—This compound is prepared by passing chlorine, at a red heat, over an intimate mixture of (prot-) oxide of uranium and charcoal, when it condenses in the cool part of the tube in dark green octohedra, possessing a metallic lustre. It is deliquescent, and forms a green aqueous solution.

Oxychloride of Uranium or *Chloride of Uranyle* (U_2O_5Cl) is formed as a yellow, deliquescent, crystalline compound, when chlorine is passed over (prot-) oxide of uranium at a red heat; its vapor has an orange-yellow color. Chloride of uranyle combines with the chlorides of potassium and ammonium, forming the crystalline compounds $U_2O_5Cl \cdot KCl + 2Aq$, and $U_2O_5Cl \cdot NH_4Cl + 2Aq$.

Subchloride of Uranium (U_2Cl_2) is formed when the (proto-) chloride is heated in a current of hydrogen. It dissolves in water, yielding a purple solution, which, after a time, becomes green, hydrogen being disengaged, and (proto-) chloride of uranium reproduced.

When sesquioxide of uranium is treated with hydrochloric acid, the compound U_2O_5Cl is produced, which speaks strongly in favor of the existence of uranyle:—



Little is known of the *sulphides of uranium*; the *sesquisulphide* appears to be a sulphur-acid, forming sulphur-salts with the sulphur-bases.

REACTIONS OF SESQUIOXIDE OF URANIUM.—*Potassa, soda, and ammonia*; yellow precipitates, insoluble in excess.

Alkaline Carbonates; yellow precipitates, soluble in excess, and reprecipitated on boiling.

¹ Another method of extracting uranium from its ores, applicable on a large scale, consists in mixing the powdered pitchblende with half its weight of quicklime, and roasting for several hours in a reverberatory furnace. The mass is treated with dilute sulphuric acid, the copper and antimony precipitated by metallic iron, and the solution mixed with a large quantity of water, which precipitates the basic sulphate of sesquioxide of uranium.

Or, the powdered ore may be treated with a mixture of sulphuric and nitric acids, the excess of acid expelled by heat, and the perfectly dry mass treated with water, which extracts the whole of the sulphate of uranium, leaving the silica and insoluble sulphates. The clear liquid is poured into a hot solution of carbonate of soda, with constant agitation, until the alkaline reaction is nearly destroyed. The solution is filtered and boiled, when carbonate of lime, magnesia, and copper are precipitated. The sesquioxide of uranium is now separated from the solution, by slightly acidifying the boiling solution with hydrochloric or sulphuric acid.

Phosphate of Soda; white precipitate.

Ferrocyanide of Potassium; red-brown precipitate.

Sulphide of Ammonium; black sulphide of uranium.

With *borax*, in the outer flame, a greenish-yellow bead, which becomes green in the inner flame.

Organic matter interferes with the precipitation of sesquioxide of uranium by alkalis.

IRON.

Sym. Fe. Eq. 28.

§ 225. In describing this most important of metals, we shall adopt a course which it is our intention to pursue with all metals in common use, viz., that of giving first a purely chemical history of the metal and its compounds, reserving for subsequent consideration the smelting of its ores, and the various forms in which the metal is found in commerce, as well as those properties which belong rather to a technical than to a chemical work.

Preparation.—In order to obtain iron in a state of purity, a quantity of piano-wire (which is contaminated only with traces of carbon) is made up into small bundles, which are oxidized at the surface by heating to redness in a current of steam; these bundles are introduced into a porcelain crucible, and covered with a quantity of powdered green glass (free from lead); the porcelain crucible is now inclosed within a Hessian crucible, and exposed to the highest temperature of a wind furnace; the carbon contained in the iron wire is oxidized at the expense of the superficial coating of oxide, and the excess of the latter dissolves in the fused glass, leaving the pure iron in the form of a button at the bottom of the crucible.

For the ordinary purposes of the chemist, however, pure iron is best prepared by reducing the *sesquioxide of iron* by means of hydrogen.

This oxide is obtained by precipitating the sesquichloride by excess of ammonia, heating, and washing the precipitate, first by decantation, and subsequently upon a filter, until the washings are free from chlorine; the precipitated hydrate is then dried at a sand-heat, reduced to powder, and introduced into a tube of hard glass drawn out to a point at one extremity, and connected at the other with an apparatus for the disengagement of pure hydrogen: when the apparatus is filled with the latter gas, the tube is heated with a spirit-lamp as long as any vapor of water is disengaged; the metal is thus obtained as a dark gray powder, which is pyrophoric; but if the reduction be effected at a very high temperature, this is not the case.

The button of pure iron is white, and possesses a silvery lustre.

General Properties of Iron.—Iron generally presents a dusky-gray color and a rather feeble lustre, which is, however, greatly increased by polishing, for iron is possessed of considerable hardness.

Its iron varies in specific gravity between 7.7 and 7.9.

Iron is a malleable metal, and exceeds all others in tenacity; an iron wire of $\frac{1}{4}$ inch in diameter is capable of supporting 705 lbs.

Iron is essentially magnetic at ordinary temperatures, but loses this character entirely at a very high temperature.

This metal is not affected by the air or oxygen at the ordinary temperature; when heated in air it is covered with a film of oxide, which presents an irides-

The oxidation process is not enhanced by the presence of alumina; a mixture of this description soon takes the appearance of a *Regulus*.

cent appearance, and changes in color as it increases in thickness; the oxidation takes place rapidly at a red heat, and a compound of (prot-) oxide and sesquioxide of iron is produced. Iron undergoes a rapid combustion when heated to whiteness in a forge, and we have already become acquainted with its combustion in oxygen gas; in both these cases, the above-mentioned proto-sesquioxide is produced. The combustion of iron in air is also witnessed when a piece of this metal is violently struck with a flint, whereby small particles of metal are detached and raised, by the heat evolved in the stroke, to the temperature at which they burn in the air.

Iron is rapidly oxidized when exposed to moist air; it becomes covered with a film of red-brown, hydrated sesquioxide of iron, commonly termed *rust*. Iron does not rust under water containing minute quantities of the alkalis or their carbonates. It has been observed that the rusting of iron proceeds much more rapidly after the first spot of rust is formed, since this forms the negative pole of a voltaic couple, of which the iron is the positive pole, and which is capable of decomposing water, eliminating hydrogen, which, in its nascent state, is also said to combine with the nitrogen of the air, forming the ammonia which is always contained in the rust of iron, and may be elicited by heating the latter with potassa. Iron is more rapidly oxidized in air containing carbonic acid than in pure air.

A very high temperature is requisite for the fusion of iron; its fusing point, in fact, can only be attained in a good wind-furnace, but it becomes soft long before it fuses, and is then capable of being easily welded. If iron be allowed to cool gradually from a state of fusion, it deposits cubical, or octohedral crystals.

Iron combines directly with most of the non-metallic elements. We have already seen that this metal is capable of decomposing steam at a red heat.

The strongest nitric acid acts but feebly upon iron, but when it is somewhat diluted, the metal is oxidized and dissolved very rapidly, nitrate of sesquioxide of iron being formed, and an inferior oxide of nitrogen disengaged. In nitric acid of a certain strength, iron dissolves without apparent evolution of hydrogen, since this gas, in its nascent state, is capable of decomposing the nitric acid, yielding nitrate of ammonia.

Iron which has been plunged into very strong nitric acid, is found to be unaffected by the dilute acid, and the same is observed with an iron wire, one end of which has been heated to redness. In both these cases, the iron is said to have assumed the *passive* state; and if, when in this condition, it be made the positive pole of a galvanic battery, it will be found that it does not combine with the oxygen which is liberated at its surface.¹ Hydrochloric acid acts energetically upon iron, chloride of this metal being formed, and hydrogen liberated. The other strong hydrogen-acids have the same effect.

When iron is heated with concentrated sulphuric acid, it is oxidized at the expense of the latter, sulphurous acid being evolved, and sulphate of (prot-) oxide of iron produced.² Dilute sulphuric acid dissolves iron with disengagement of hydrogen.

IRON AND OXYGEN.

(Prot-) oxide of iron	FeO
Sesquioxide of iron	Fe ₂ O ₃
Ferric acid	FeO ₃
(Magnetic oxide of iron	Fe ₃ O ₄)

¹ This curious phenomenon has been attributed in a plausible manner to the formation of a protecting film of oxide upon the surface of the metal, but this explanation does not account for all the properties of iron in its passive state.

² Or, according to Levol, sulphate of sesquioxide.

The last of these is inclosed in parentheses, because it is not an independent oxide.

OXIDE, OR PROTOXIDE OF IRON.

FeO. Eq. 86.

§ 226. This oxide has never been obtained in the pure state; it is precipitated as a white hydrate, when solution of potassa is added to solution of (proto-) sulphate of iron; the precipitate, however, very readily absorbs oxygen from the air, being converted, first into the green hydrated magnetic oxide, and ultimately into red-brown hydrated sesquioxide of iron. If the two solutions be mixed in a state of ebullition, and the mixture be then boiled, a black precipitate is formed, which appears to be the anhydrous oxide of iron, but it is impossible to collect it without its suffering oxidation; it even decomposes water at the boiling point, eliminating hydrogen.

Hydrated (prot-) oxide of iron dissolves in ammonia, but the solution rapidly deposits the sesquioxide when exposed to air.

This oxide is a very powerful base, and forms well-defined salts.

NITRATE OF (PROT-) OXIDE OF IRON, PROTONITRATE OF IRON.

FeO.NO₃.

When iron is dissolved in cold dilute nitric acid, and the solution carefully concentrated, crystals of a *double nitrate of oxide of iron and oxide of ammonium* are deposited.

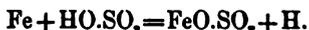
The nitrate of oxide of iron is best prepared by decomposing the sulphate with nitrate of baryta.

It is of a green color, and crystallizes with difficulty. Its aqueous solution is decomposed by ebullition, depositing a basic salt of the sesquioxide; the solution must therefore be concentrated *in vacuo*.

SULPHATE OF (PROT-)OXIDE OF IRON, PROTOSULPHATE OF IRON, commonly called SULPHATE OF IRON, COPPERAS, and GREEN VITRIOL.

FeO.SO₃.

§ 227. This salt is found when iron, or sulphide of iron, is dissolved in dilute sulphuric acid:—



Preparation.—It is generally prepared from the mineral known as *iron-pyrites*, FeS₂. This mineral is strongly heated in a retort, in order to separate part of the sulphur which it contains; the residue is then exposed to the action of air and moisture, when it absorbs oxygen, and is converted into sulphate of oxide of iron; the mass is exhausted with water, and the solution evaporated to crystallization.¹

It will be remembered that a considerable quantity of this salt is obtained in the manufacture of alum (*see* § 211).

Properties.—Pure sulphate of iron has a slightly bluish-green color; it forms oblique rhomboidal prisms, which are transparent, and have the composition FeO.SO₃.HO+6Aq. When exposed to air, these soon become covered with an ochreous crust of a *basic sulphate of sesquioxide of iron* (2Fe₂O₃.SO₃) from absorption of oxygen:—



The crystals lose 6 eqs. water of crystallization at 212° F. (100° C.), and fall to

¹ Any copper which may be present in the crude lye is precipitated by means of metallic iron.

a grayish-white powder (*Ferri sulphas exsiccatum*), which dissolves gradually when treated with water; at a higher temperature, the last equivalent of (constitutional) water begins to go off, but cannot be thoroughly expelled without partial decomposition of the salt. After strongly heating, the sulphate is almost insoluble in water, but dissolves in nitric acid.

At a pretty strong red heat, sulphate of iron is completely decomposed, sesquioxide of iron (*colcothar*) being left, and sulphurous acid, together with anhydrous sulphuric acid, passing off:—



since a little water is always present, the sulphuric acid is obtained in the receiver as a hydrate (*see Nordhausen Sulphuric Acid*, p. 159).

The crystals of sulphate of iron dissolve in 2 parts of cold and in $\frac{1}{2}$ -part of boiling water; the solution has a pale green color; it is perfectly neutral, and of a nauseous metallic taste. When exposed to the air, solution of sulphate of iron deposits a dirty-brown basic sulphate of sesquioxide ($2\text{Fe}_2\text{O}_3.\text{SO}_3$), the neutral sulphate of sesquioxide ($\text{Fe}_2\text{O}_3.3\text{SO}_3$) remaining in solution (*see* the above equation). If a solution of sulphate of iron be mixed with a slight excess of sulphuric acid, and crystallized at a temperature of 176° F. (80° C.), the formula of the crystals is $\text{FeO}.\text{SO}_3.\text{HO} + 3\text{Aq}$. If a large excess of sulphuric acid be present, the crystals are $\text{FeO}.\text{SO}_3.\text{HO} + 2\text{Aq}$. On adding alcohol to solution of sulphate of iron, a white precipitate is obtained, which is $\text{FeO}.\text{SO}_3.\text{HO}$; the same salt is obtained with concentrated sulphuric acid. The sulphate of iron is easily converted into sulphate of sesquioxide by oxidizing agents (*e. g.* chlorine, nitric acid). Sulphate of iron in solution (like all other protosalts of iron) is capable of absorbing the binoxide of nitrogen, forming a brown solution, which contains just so much of the binoxide of nitrogen that its oxygen would suffice to convert into sesquioxide all the (prot-)oxide of iron present.

Three varieties of sulphate of iron are met with in commerce; *viz.* 1. The pale green crystals which have been deposited from neutral solutions. 2. The bluish-green crystals obtained when the solution is acid; and 3. The bright green crystals formed in liquids which have been long exposed to the air; the difference of color appears to be due to the sulphate of sesquioxide of iron which is present.

The sulphate of iron prepared on the large scale is generally contaminated with sulphates of copper, zinc, manganese, alumina, magnesia, and lime; the manufacturer generally separates the copper by digesting the iron-liquor with scraps of metallic iron.

Uses.—This salt is very largely employed by dyers and calico-printers, for it is the basis of several mordants and colors, and serves, moreover, for the preparation of others; thus, it is employed for the preparation of Prussian blue, and of white or reduced indigo, where the deoxidizing properties of the salt are turned to advantage.

The use of sulphate of iron for the preparation of fuming sulphuric acid and of colcothar, has already been alluded to. A considerable quantity is consumed in the preparation of ink. It is also used in the laboratory as a reducing agent.

Sulphate of iron is also an important medicinal agent. For this use it is highly important that it should contain no sulphate of copper, which may be shown by adding a few drops of dilute sulphuric acid, and immersing a bright steel knife-blade in it, which would become covered with a film of metallic copper after the lapse of a few minutes.

The sulphate of (prot-) oxide of iron is capable of forming double-salts, in which the water of constitution in the sulphate is replaced by sulphate of potassa, soda, ammonia, or oxide of manganese; these salts crystallize with 4 equivalents of water; the potassa-salt, however, contains 6 equivalents, unless deposited from

acid solutions. It is isomorphous with the corresponding compound of sulphate of potassa and sulphate of magnesia.

CARBONATE OF (PROT-) OXIDE OF IRON, PROTOCARBONATE OF IRON.



This carbonate is found in abundance in England, where it forms the well-known *spathic ore*, the principal ore of iron. It often forms rhombohedral crystals, which are very slowly acted upon by acids. Crystals resembling these may be prepared by decomposition of sulphate of iron with carbonate of soda, at a high temperature, in a sealed tube.

Carbonate of protoxide of iron is obtained as a white hydrate, when a solution of sulphate of iron is mixed with an alkaline carbonate; it becomes, however, rapidly green, being converted into hydrate of magnetic oxide of iron (Fe_3O_2) with evolution of carbonic acid:—



it is in this state that the iron exists in the *mistura ferri composita*.

When (proto-) carbonate of iron is heated in a retort, carbonic oxide and carbonic acid are disengaged, and magnetic oxide of iron (Fe_3O_2) left:—



(Proto-) carbonate of iron is dissolved by water holding carbonic acid in solution, which accounts for the presence of this salt in mineral waters. When such a solution is exposed to the air, it absorbs oxygen, and deposits sesquioxide of iron.

SESQUIOXIDE, PEROXIDE, OR RED OXIDE OF IRON.



§ 228. This oxide is found very abundantly in nature, generally crystallized; we shall have to refer to it again, when describing the ores of iron.

It has been already stated that sesquioxide of iron may be obtained by calcining the (proto-) sulphate; the residue, which has a fine red color, is termed *colcothar*, and is employed in painting, and for polishing plate glass.

The residue left on igniting the nitrate of sesquioxide of iron consists of a nearly black variety of this oxide.

Hydrated Sesquioxide of Iron ($\text{Fe}_2\text{O}_3.3\text{HO}$) is obtained as a red brown precipitate, when an alkali is added to a solution of a salt of sesquioxide of iron; it is usually prepared by dissolving sulphate of iron in water, adding a quantity of dilute sulphuric acid, and boiling with successive additions of nitric acid, till no more red fumes are evolved; in this way the sulphate of (prot-) oxide is converted into sulphate of sesquioxide of iron:—



and if ammonia in excess be now added to the solution, a precipitate of hydrated sesquioxide of iron is obtained:—



this precipitate should be collected upon a calico filter, and washed with hot water till the washings are no longer precipitated by chloride of barium. It should be dried at a temperature not exceeding 180° F. (82° C.)

The hydrated sesquioxide of iron is easily rendered anhydrous. Other hydrates of sesquioxide of iron, of the formulæ $\text{Fe}_2\text{O}_3.\text{HO}$ (*brown iron ore, needle-iron ore*), $2\text{Fe}_2\text{O}_3.3\text{HO}$ (*fibrous brown iron ore, or brown hæmatite, and compact brown iron ore*), and $\text{Fe}_2\text{O}_3.2\text{HO}$ (another variety of brown iron ore).

Sesquioxide of iron, when heated nearly to whiteness, evolves oxygen, and is converted into the *magnetic oxide*, Fe_3O_2 , and hence the reason that this latter,

and not the sesquioxide, is formed when iron is burnt in oxygen. If sesquioxide of iron be heated to redness in a stream of hydrogen or carbonic oxide, it is first reduced to the magnetic oxide, and afterwards to the metallic state.

Sesquioxide of iron, when calcined, exhibits a sudden incandescence, and is converted into a modification which is almost insoluble in nitric and sulphuric acids, and dissolves but slowly in hydrochloric acid.

The sesquioxide is not so powerful a base as the protoxide of iron, and appears occasionally to be capable of playing the part of an acid, since it retains potassa and soda with great obstinacy, when precipitated from its solutions by these alkalies, and it is said that true compounds of these latter with the sesquioxide may be obtained.

Salts of sesquioxide of iron, like those of alumina, have generally an acid reaction.

Uses.—Sesquioxide of iron is sometimes employed for coloring glass.

It is used medicinally in various forms.

The *ferris sesquioxidum* of the London Pharmacopœia (formerly called *ferris sesquicarbonas*) is a variable mixture of sesquioxide with protocarbonate and protoxide of iron, formed by the oxidizing action of air upon the carbonate of iron precipitated by mixing carbonate of soda and sulphate of iron in solution.

Ferris oxidum rubrum of Edinburgh is a similar compound, whilst that of Dublin is merely colcothar.

Rubigo ferri is simply rust.

The hydrated sesquioxide of iron is employed as an antidote in cases of poisoning by arsenic.

NITRATE OF SESQUIOXIDE OF IRON, $\text{Fe}_2\text{O}_3 \cdot 3\text{NO}_3$.

This salt may be obtained by dissolving iron in nitric acid, with the aid of heat, or by dissolving the hydrated sesquioxide in that acid.

It crystallizes in yellowish four-sided rectangular prisms, which are easily decomposed by heat, and are very soluble in water.

The basic nitrates of sesquioxide of iron have been little studied.

SULPHATE OF SESQUIOXIDE OF IRON,¹ $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$.

The sulphate of sesquioxide of iron is produced, according to Level, when concentrated sulphuric acid acts upon iron, with the aid of heat:—



It may be prepared by heating either metallic iron or sulphate of iron with concentrated sulphuric acid, and expelling the excess of acid by heat. The dirty-white residue thus obtained can only be dissolved by protracted digestion with water.

It is also prepared (as already indicated) by oxidizing the sulphate of iron with nitric acid (see hydrated sesquioxide of iron); the solution is mixed with a little sulphuric acid, and evaporated to dryness.

The formula of the sulphate of sesquioxide of iron thus obtained, if not too strongly heated is $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 + 9\text{Aq}$. The salt is naturally very soluble in water, but after drying, it dissolves with difficulty. Its solution, if pretty dilute, deposits *basic sulphate* when boiled.

Several *basic sulphates* are known.

The most important, which has been above mentioned as resulting from the action of the air on the (proto-) sulphate, has the composition $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$, and is employed in painting on glass and porcelain.

It occurs in nature, with 6 equivalents of water, as *vitriol-ochre*.

¹ This salt has been found native, as *coquimbite*.

The sulphate of sesquioxide of iron, like those of alumina and sesquioxide of chromium, combines with sulphates of the alkalis to form alums.

Potassa Iron-Alum may be prepared directly from its constituent salts; it may be crystallized, though with some difficulty, in nearly colorless octohedra, of the formula $\text{KO.SO}_3, \text{Fe}_2\text{O}_3, 8\text{SO}_3 + 24\text{Aq}$.

PHOSPHATE OF SESQUIOXIDE OF IRON is formed as a white precipitate, when solution of common phosphate of soda is added to sesquichloride of iron; its formula is said to be $\text{Fe}_2\text{O}_3, \text{PO}_5 + 4\text{Aq}$.

This salt occurs in certain iron ores, and much injures the quality of the metal obtained from them, which is found to contain phosphorus, rendering it brittle.

The phosphate of sesquioxide of iron has been employed medicinally.

No pure carbonate of sesquioxide of iron has yet been obtained; when a salt of the sesquioxide is decomposed by an alkaline carbonate, carbonic acid is disengaged, and hydrated sesquioxide of iron precipitated. The hydrated sesquioxide dissolves in the alkaline bicarbonates, yielding red solutions, which appear to contain double carbonates of the alkalis and of sesquioxide of iron; these solutions are not decomposed by boiling.

Several silicates of sesquioxide of iron are found in the mineral kingdom. *Anthosiderite* has the formula $\text{Fe}_2\text{O}_3, 3\text{SiO}_2 + \text{Aq}$; *hisingerite*, $\text{FeO.SiO}_2, \text{Fe}_2\text{O}_3, \text{SiO}_2 + 6\text{Aq}$.

MAGNETIC OXIDE, OR BLACK OXIDE OF IRON.

(*Proto-sesquioxide of Iron, Ferroso-ferric Oxide.*)



§ 229. This oxide occurs in nature in the form of the *loadstone*, and constitutes a very important ore of iron. It is often met with in fine octohedral crystals. It may be obtained in a pure state by exposing fine iron wire to the action of steam at a red heat; it then forms minute octohedra, which are highly magnetic.

The *hydrated magnetic oxide* may be prepared by dividing an aqueous solution of sulphate of iron into three equal parts, peroxidizing two of these with nitric acid, adding the other, and pouring the mixture, with frequent stirring, into an excess of solution of ammonia; if the operation were reversed, and the ammonia added to the mixture, the sesquioxide would be first precipitated, then the (prot-)oxide, so that a *mixture*, and not a *combination* of the two, would be obtained.

The hydrated magnetic oxide has a dark-green color, and is attracted by the magnet.

It appears that the magnetic oxide of iron is a compound of the (prot-) oxide with the sesquioxide, for if it be dissolved in an acid, the solution gives the reactions of both these oxides, and when an alkali is gradually added, the sesquioxide is first precipitated.

The black oxide of iron, known as *smithy scales*, from their being detached in the forging of iron, varies in composition according to the circumstances under which it is formed, but always contains both sesquioxide and (prot-) oxide of iron.

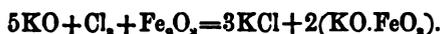
FERRIC ACID, FeO_3 .

This acid has not been obtained in the separate state; several of its salts have, however, been examined.

FERRATE OF POTASSA may be obtained by oxidizing iron-flings with nitre at a very high temperature.

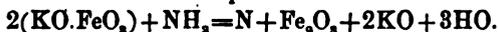
A better method of preparing it consists in passing a current of chlorine

through a very concentrated solution of potassa, in which hydrated sesquioxide of iron is suspended:—



The operation is terminated when the black precipitate which is formed dissolves perfectly in water. This black precipitate is the ferrate of potassa, which may be freed from alkali by draining on a porous tile.

The salt is insoluble in strong alkaline solutions, but very soluble in water, giving a fine red liquid; it is a very unstable salt, for even when its solution is evaporated *in vacuo*, it is decomposed into potassa, sesquioxide of iron, and oxygen, so that it has never been crystallized. The above decomposition is very easily effected by heat, by organic matters, and by (even the weakest) acids. Even ammonia reduces the ferrate of potassa:—



Ferrate of Soda resembles the potassa-salt. The *ferrates of baryta, strontia, lime, &c.*, may be obtained by double decomposition; they have a fine red color, and are insoluble.

§ 230. NITRIDE OF IRON.—The compound of iron with nitrogen is little known; it is said to be formed when iron is heated to redness for some time in a current of ammonia, the metal becoming white and brittle. A similar (perhaps identical) product is obtained by passing ammonia over (proto-) chloride of iron, when a silvery-white, lustrous, spongy mass remains.

(PROTO-) CHLORIDE OF IRON, FeCl .

The anhydrous (proto-) chloride is prepared by passing hydrochloric acid gas over iron at a red heat, when it is obtained as a brown, fused mass, which crystallizes on cooling, and sublimes, at a higher temperature, in yellowish crystals.

This compound is sometimes employed as a source of pure iron; for when heated in a current of hydrogen, it yields this metal in crystals.

By dissolving iron in a slight excess of hydrochloric acid, and evaporating the solution, pale green, oblique, rhomboidal prisms are obtained, the formula of which is, $\text{FeCl} + 4\text{Aq}$.

(Proto-) chloride of iron is very soluble in water and alcohol; it is capable of forming double-salts with the chlorides of potassium and ammonium.

SESQUICHLORIDE, OR PERCHLORIDE OF IRON, Fe_2Cl_3 .

To obtain this salt in the anhydrous state, coils of iron wire may be introduced into a tube of hard glass, and moderately heated in a pretty abundant supply of chlorine. It then sublimes in brown, crystalline scales, which are deliquescent, and very soluble in water, alcohol, and ether, yielding red-brown solutions.

Hydrated sesquichloride of iron is prepared by dissolving iron in a mixture of hydrochloric and nitric acids, or by treating the sesquioxide with hydrochloric acid. On evaporating the solution, yellow scaly crystals may be obtained, of the formula $\text{Fe}_2\text{Cl}_3 + 5\text{Aq}$. When these are heated, they evolve hydrochloric acid, and a compound of sesquichloride with sesquioxide of iron remains. A similar compound is deposited as a brown precipitate, when a solution of sesquichloride of iron suffers spontaneous decomposition, or when it is boiled for some time.

The alcoholic and ethereal solutions of this salt are decolorized by exposure to light, (proto-) chloride being formed, together with products of oxidation of alcohol or ether.

Sesquichloride of iron is decomposed by vapor of water at a red-heat, hydrochloric acid and crystallized sesquioxide of iron being produced:—



This salt is used medicinally, in the form of tincture (alcoholic solution). It is also a useful reagent.

If a solution of sesquichloride of iron be mixed with chloride of potassium, or chloride of ammonium, and evaporated, fine red crystals are obtained, of the formulæ, respectively :—



The latter salt is employed in medicine, under the name of *ammonio-chloride of iron*.

The *Bromides of Iron* correspond in composition to the chlorides, and may be prepared in a similar manner.

IODIDE, OR PROTIODIDE OF IRON, FeI.

Preparation. In order to prepare this salt, a quantity of iodine is mixed with water, one-third of its weight of iron filings added, and the whole digested for some time, in a flask, at a gentle heat; the clear liquid is poured off, the residue in the flask washed with hot water, the washings being added to the solution, and the whole evaporated in contact with iron, at a heat, not exceeding 212° F.

Properties.—Iodide of iron is very soluble in water, yielding a pale green solution, from which, by careful evaporation, greenish crystals may be obtained, of the formula $\text{FeI} + 4\text{Aq}$. When the aqueous solution is exposed to air, it absorbs oxygen, part of the iron being converted into sesquioxide, and yielding its iodine to another portion of the iodide, producing a sesqui-iodide, which is precipitated in combination with the sesquioxide as a brown powder :—



In order to avoid this, a long turning of iron, or a coil of clean iron wire should be kept in the solution.

When gently heated, iodide of iron fuses, and on cooling, solidifies to a gray crystalline mass, which has a metallic lustre and is deliquescent. If it be strongly heated with free access of air, the iodine is expelled, and the iron converted into sesquioxide.

The iodide of iron is largely used in medicine, and is sometimes employed for the preparation of iodide of potassium.

The *Sesqui-iodide of Iron* (Fe_2I_3) may be prepared by dissolving the hydrated sesquioxide in hydriodic acid, or by treating iron with excess of iodine; it has a red color, is volatile, deliquescent, and soluble in water and alcohol.

IRON AND SULPHUR.

(Proto-) sulphide	FeS
Sesquisulphide	Fe_2S_3
Bisulphide	FeS_2
Tersulphide	FeS_3

§ 231. Two *subsulphides of iron* also exist; Fe_2S , prepared by reducing the basic persulphate of iron by hydrogen, and Fe_3S , which is formed when hydrogen acts upon the anhydrous (proto-) sulphate. Both these dissolve in acids, evolving hydrogen and sulphuretted hydrogen, and producing proto-salts of iron.

SULPHIDE OF IRON. PROTOSULPHIDE OF IRON. SULPHURET OF IRON.



This compound is occasionally met with in nature.

Preparation.—It may be prepared by the direct combination of iron and sulphur; this combination may even take place at the ordinary temperature; a mixture of sulphur and iron filings, if kept for some time in a moist state, become converted into sulphide of iron; such a mixture is sometimes called *Lemery's volcano*; the combination takes place with considerable evolution of heat, and if the mixture be buried in sand it forms a sort of mimic volcano.

The best method of preparing sulphide of iron, however, consists in projecting, by small portions at a time, into a red-hot crucible, an intimate mixture of 30 parts of iron-filings with 21 parts of flowers of sulphur, always waiting till one portion has combined before adding another.

A hydrated (proto-) sulphide of iron is obtained when a solution of a proto-salt of iron is mixed with an alkaline sulphide.

Properties.—(Proto-) Sulphide of iron is a dark gray substance, having a metallic appearance; it is easily oxidized when exposed to moist air, being converted into sulphate of the (prot-) oxide; when large masses of sulphide are oxidized in this way, sufficient heat is often evolved to set fire to the rest of the mass, and hence the dangerous fires in coal-mines where large quantities of this mineral exist.

When heated with free access of air, sulphurous acid is evolved, and the iron converted into magnetic oxide.

Sulphide of iron is perfectly insoluble in water, but dissolves in most acids, with evolution of sulphuretted hydrogen, and production of a proto-salt of iron:—



The hydrated sulphide of iron forms a black precipitate, which, when exposed to the air, is very rapidly converted into sulphate. It is somewhat soluble in alkaline sulphides, but is precipitated from the solutions by boiling; the hydrate dissolves very easily in most acids.

Uses.—Sulphide of iron is very largely used in the laboratory, for the evolution of sulphuretted hydrogen. The hydrated sulphide has been recommended as an antidote to corrosive sublimate and the salts of lead and copper; it is prepared for this purpose by precipitating solution of sulphate of iron with sulphide of ammonium, collecting on a cloth filter, and washing rapidly with hot water till the washings are no longer precipitated black by acetate of lead; the moist sulphide is then preserved in well-stoppered bottles.

SESQUISULPHIDE OF IRON, Fe_2S_3 .

This sulphide is found in nature associated with the sulphide of copper, in copper-pyrites. It may be prepared by decomposing sesquioxide of iron by sulphuretted hydrogen at 212° F. (100° C.) It forms a grayish mass, which is decomposed when heated in close vessels, sulphur being evolved, and *magnetic pyrites* (Fe_3S_4) left.

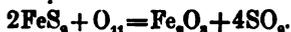
The sesquisulphide of iron is obtained as a black precipitate, when a solution of sesquioxide of iron is added to an alkaline sulphide; if the experiment be reversed, a mixture of (proto-) sulphide of iron and sulphur is precipitated.

BISULPHIDE OF IRON. IRON PYRITES. MARTIAL PYRITES.



The bisulphide of iron is found abundantly in nature in a crystallized state, often in well-defined cubes and dodecahedra. Its specific gravity is 4.98. It

has a fine brass-yellow color, and metallic lustre. It is generally unalterable in air at the ordinary temperature, but when roasted in air it disengages sulphurous acid, and is converted into sesquioxide of iron :—



When heated in close vessels, it gives up a part of its sulphur, and leaves magnetic pyrites.

Some varieties of iron pyrites are oxidized by exposure to moist air, being converted into sulphate of iron and sulphuric acid; this property is generally attributed to the presence of an inferior sulphide.

Bisulphide of iron is not affected by water or by hydrochloric acid. Nitric acid converts it into sulphate of sesquioxide of iron, with separation of sulphur, unless the acid be very concentrated. Boiling concentrated sulphuric acid also dissolves it, sulphurous acid being disengaged.

The bisulphide may be obtained artificially by heating the (proto-) sulphide with half its weight of sulphur, when it is left as a yellow powder.

Yellow octohedral crystals, resembling iron pyrites, may be obtained by heating a mixture of sesquioxide of iron, sulphur, and sal-ammoniac, in a sand-bath, to the temperature at which the latter is volatilized. It is also formed when the sesquioxide is acted on by sulphuretted hydrogen at a temperature exceeding 212° F.

Iron pyrites is employed as a source of sulphur; it is also, as before mentioned, turned to account in the preparation of alum and of various compounds of iron (green vitriol, &c.)

MAGNETIC PYRITES, $\text{Fe}_3\text{S}_2 = \text{FeS}_2 + 6\text{FeS} = \text{Fe}_2\text{S}_3 \cdot 5\text{FeS}$.

This variety of pyrites, named from its magnetic properties, is found in nature in six-sided prisms of a bronze color. It is much more easily oxidized than the bisulphide, and evolves sulphuretted hydrogen when treated with sulphuric acid. It is always formed when either of the oxides of iron is strongly heated with an excess of sulphur, or when iron at a white heat is brought in contact with sulphur.

Another variety of magnetic pyrites, corresponding in composition to the magnetic oxide, is said to exist, its formula being Fe_3S_4 .

The *Tersulphide of Iron*, FeS_3 , is not known in the separate state, but is said to be obtained in combination with sulphide of potassium when sulphuretted hydrogen is passed into a solution of ferrate of potassa in potassa; the tersulphide is decomposed, with separation of sulphur, when an attempt is made to isolate it.

SUBPHOSPHIDE OF IRON, Fe_3P .

This compound may be obtained by reducing the phosphate of (prot-) oxide of iron with charcoal at a high temperature; it is a gray, very hard, fusible substance. The presence of a very small quantity of this substance in a specimen of iron is capable of rendering it brittle, and hence unfit for the purposes of bar-iron.

IRON WITH CARBON.

§ 232. Only one carbide of iron of definite composition is known; this is obtained when ferrocyanide of potassium is calcined in close vessels, and the cyanide of potassium washed out of the residue with water; the black compound thus obtained has the composition, FeC_3 ; when heated in contact with air, it is converted into sesquioxide of iron and carbonic acid.

When iron is heated in contact with carbon, it never takes up more than six per cent., which would cause the compound to approach to the formula Fe_3C .

However, much smaller quantities of carbon are capable of giving rise to a notable alteration in the properties of the metal, a circumstance which will be further considered when we treat of the metallurgy of iron.

When iron containing carbon is dissolved in hydrochloric acid, a peculiar compound of carbon and hydrogen is evolved, which communicates a nauseous odor to the hydrogen thus produced.

A *boride of iron* has been obtained by reducing the borate of iron by hydrogen.

IRON WITH SILICON.—A compound of these elements may be obtained by strongly heating a mixture of iron filings, silicic acid, and carbon; the mass thus obtained has a metallic appearance, is malleable, and contains 9 or 10 per cent. of silicon. Most varieties of the iron of commerce contain 1 or 2 per cent. of silicon. When treated with acids, the silicide of iron is decomposed, leaving a residue of silica.

METALLURGY OF IRON.

§ 233. The following are the chief forms in which this metal is found in nature.

Meteoritic Iron, as its name implies, occurs in the metallic masses which occasionally fall upon the earth, and are known as *aeroliths*, or *meteoric stones*; in these, it is associated, in the metallic state, generally with cobalt, nickel, manganese, and some other metals, and with certain nonmetallic substances, as sulphur, carbon, phosphorus, and silicon.

Sesquioxide of iron, in the anhydrous state, is found in several minerals.

Oligist or specular iron (iron-glance), Fe_2O_3 , occurs in rhombohedral crystals, which possess a certain metallic lustre, and spec. grav. 5.22. It usually contains a small quantity of the magnetic oxide. This mineral occurs chiefly in Elba.

Micaceous iron consists also of sesquioxide; it is found in thin, hexagonal tables, with metallic lustre.

Red hæmatite (sometimes called *blood-stone*) is another form of the sesquioxide, occurring generally in reniform masses of a radiated fibrous structure; its spec. grav. is about 5, and its hardness very considerable; this latter property renders it useful for burnishing. Hæmatite has a brownish-red color, which changes, under some aspects, to steel-gray; its powder is red.

Brown hæmatite is a hydrated sesquioxide of iron: its form is similar to that of the red hæmatite.

Étite, kidney-form clay-ironstone, or eagle-stone forms globular masses, consisting of hydrated sesquioxide of iron associated with clay.

Oolitic iron-ore has a similar composition, and is found in small round grains, aggregated together, like the milt of a fish, whence its name.

The ores known as *morass-ore, swamp-ore, and meadow-ore*, consist of hydrated sesquioxide of iron.

Magnetic iron-stone (Fe_3O_4) is found chiefly in Sweden; its color is dark gray, and spec. grav. about 5.¹

Iron-sand, which has a black color and metallic lustre, is composed chiefly of the magnetic oxide; it generally contains titanium.

The mineral termed *umber*, which is used as a pigment, consists of the hydrated oxides of iron and manganese.

¹ Andrews has recently examined a specimen of this ore, in which part of the protoxide of iron was replaced by magnesia.

The two varieties of pyrites, viz. *magnetic pyrites* (Fe_3S_4), and *common*, or *cubical pyrites* (sometimes called *radiated pyrites*) have been already mentioned.

(*Proto*-) *Carbonate of iron* occurs in two varieties; *spathic* (or *sparry*) *iron-ore* is sometimes found in amorphous masses, and sometimes crystallized in rhombs, octohedra, and dodecahedra. Its color varies between brown and yellow, and its spec. grav. from 3.6 to 3.8. It becomes dark when exposed to air, or when heated. *Spathic iron-ore* often contains a little manganese. The other variety, *common clay-iron-stone* (*black-band*) is yellow, or red-brown, and varies in spec. grav. from 2.9 to 3.5; it is generally, as its name imports, associated with clay.

The above minerals, though containing iron in abundance, are not all made use of for the extraction of iron, and therefore should not, strictly speaking, be designated *ores* of that metal.

In this sense, the only true *ores of iron* are, *the magnetic oxide*, *the anhydrous sesquioxide*, *the hydrated sesquioxide*, and *the (proto-) carbonate*. The minerals containing sulphur and phosphorus are not employed, since they would yield an inferior product.

The manufacture of iron may conveniently be divided into 1. *The preparation of the ores*, 2. *the extraction of the metal*, and 3. *its purification*.

The preparation of the iron ores is very simple; the earthy ores are merely subjected to a species of rough levigation, by which the greater part of the clay is separated. Those ores which occur in rocks or large masses, *clay iron-stone*, for example, are roasted, by which the water and carbonic acid are expelled, and the ore is rendered more friable.

The extraction and purification of the iron, when the ore is very pure and rich, are sometimes effected in one process.

A large rectangular crucible is employed, the sides of which are formed of thick plates of cast-iron, and the bottom of very refractory stone; this crucible is furnished with a *tuyère*, or air-pipe, of copper, by which a rapid stream of air may be directed into the crucible. In order to charge the latter, a quantity of red-hot charcoal is thrown into the bottom, and an iron-shovel is then held so as to divide the space above the charcoal into two compartments, one of which is charged with the previously roasted mineral, and the other with charcoal; the shovel is then withdrawn, and a gradually increasing current of air supplied by the *tuyère*, whilst the workman stirs the mass; in this manner, a spongy mass of metal is obtained, which is freed from the fused slag by hammering, and is then forged into bars. The explanation of this process is simple enough; the carbon is converted into carbonic acid at the expense of the air introduced into the crucible; this carbonic acid then coming in contact with a mass of red-hot charcoal, is reduced to the state of carbonic oxide, which, in its turn, abstracts the oxygen from the iron-ore, thus reducing it to the state of metal, which is at first disseminated through the mass, and afterwards accumulated by the workman into a spongy state; the whole of the iron, however, is not reduced, for part of it, in the state of (prot-) oxide, combines with the silicic acid contained in the ore to form a fusible scoria or slag, which flows to the bottom of the crucible, whence it is drawn off from time to time.

The process lasts about six hours, and yields from 2½ cwts. to 3 cwts. of marketable iron for every 9½ cwts. of ore, with a consumption of about 10 cwts. of charcoal.

The process above described is very seldom employed, since it involves a considerable loss of metal, and can only be carried into operation with particular ores.

We shall now proceed to consider the process generally used for smelting iron-ores, which consists in converting the iron into a fusible carbide, by exposing the oxide to a very high temperature in contact with carbon, and in a subsequent purification of the resulting product.

The extraction of the metal from the ore is effected in a *blast-furnace*, which has the form of two truncated cones joined together at their bases, and is lined with very refractory brick or stone.

Air is forced into this furnace, by means of a steam-engine, through two or three *tuyère-pipes*.

In order to obtain the compound of iron with carbon in a fused state, it is of course necessary that a fusible slag should be formed which contains all the impurities of the ore. These impurities (technically termed *gangue*) consist generally of silica and alumina (combined in the form of clay), and since these are very infusible, it is necessary to add some substance which shall form a liquid combination with them at the temperature of the furnace. For this purpose, carbonate of lime is employed, which produces with the clay a double silicate of alumina and lime, fusing with comparative readiness.¹ Should the gangue consist of quartz only, the ore is mixed with an argillaceous iron-ore, and a quantity of limestone added. When the gangue consists of carbonate of lime, a proper quantity of clay, or of argillaceous ore is added. The substances thus added to promote the fusion of the slag are termed fluxes.

The carbonate of lime not only acts as a flux, but likewise prevents any loss of iron which would otherwise result from the production of a double silicate of alumina and oxide of iron, the latter base being replaced in the combination by an equivalent proportion of lime.

The operation is commenced by charging the furnace to a certain height with fuel, and, after this has fairly kindled, introducing a quantity of ore, mixed with flux, from the top of the furnace; the blast is increased gradually, and alternate layers of fuel and ore introduced from time to time. The fused combination of iron with carbon collects at the bottom of the furnace, and above it, a layer of slag; these are drawn off from time to time, through different apertures, the former being allowed to run into moulds of sand, in which it is cast into rough masses, sent into the market as *pig-iron*, or *cast-iron*. The process is not interrupted till the furnace is in want of repair.

The fuel employed in the blast-furnaces is either charcoal, wood, or coke; the latter is preferred where (as in England) coal can be obtained in abundance.

When charcoal is employed, the amount of lime present, in proportion to the clay, is so regulated that the most fusible slag shall be formed, and a lower temperature is required than when coke is employed; for, since this latter always contains more or less sulphur (as iron-pyrites), it is necessary to employ more limestone, in order to convert the sulphur into sulphide of calcium, and thus to prevent its passing into the pig-iron, the quality of which it would injure. The excess of limestone, however, renders the slag less fusible, and it becomes necessary to build the furnace higher, in order to raise the temperature to the required extent.

A considerable saving of fuel has been effected by feeding the furnace through the *tuyères* with air heated to 400° or 500° F., instead of with cold air, the air being raised to that temperature by the waste heat of the furnace. This is generally known as the *hot-blast* process.

The reactions which take place in the interior of the blast-furnace are easily followed, if we bear in mind the existence of an ascending column of atmospheric air and other gases, and of a descending column consisting of a mixture of ore, fuel, and slag. The air entering through the *tuyères*, at the lower part of the furnace, is at once deoxidized by the fuel, its oxygen being entirely converted into carbonic acid; the latter, coming in contact with another portion of heated fuel, is reduced to carbonic oxide, by which the reduction of the ore is chiefly

¹ The most fusible slag is that in which the oxygen in the acid is double that in the two bases. The presence of manganese augments the fusibility of the slag.

effected. The ore, slag, and fuel lose their moisture and carbonic acid in the higher part of the furnace; the oxide of iron is then reduced, at a lower stage, where the temperature is more elevated, by the carbonic oxide, and the earthy matters separate in the form of a fusible slag. At a still lower level in the furnace, the reduction of the iron is completed by the carbon, a portion of which also combines with the difficultly fusible iron, forming a compound which fuses at the temperature existing in that part of the furnace, and runs down into the *crucible*, where it forms a layer beneath the more fusible and lighter slag; this is allowed to run off over the side of the crucible, so that the latter becomes filled, after a time, with metallic iron.

Although hydrogen exists in every part of the blast-furnace, it has no share in the reduction of the ore, since, in its affinity for oxygen, it has been proved to be inferior to carbonic oxide.

The gas which issues from the chimney (or *tunnel*, as it is commonly called) of the blast-furnace, consists chiefly of carbonic acid, carbonic oxide, hydrogen, and nitrogen; this gas is inflammable, and has been used, in some works, for heating the steam-boilers, and for other purposes. The hydrogen, of course, arises from the decomposition of the water contained in the ore, and in the fuel, and the nitrogen, from the atmospheric air supplied to the furnace.

The *cast-iron* obtained by the above process, contains three or four per cent. of carbon and silicon, with traces of sulphur, phosphorus, and manganese; these impurities render it brittle, and hence unfit for many purposes; it must, therefore, be refined, or purified, and this is usually called the conversion of *pig-iron* into *bar-iron*.

This process may be divided into two operations, the *refining* and *puddling*. The refining furnace is constructed of iron, lined with refractory clay, and is furnished with tuyere-pipes. In this furnace, the pig-iron is kept in fusion for about two hours, under a strong blast of air: its surface is oxidized by the latter, and the mass being stirred by the workman, so as to bring all parts of it in contact with the oxide, this latter converts the carbon into carbonic oxide, and the silicon into silicic acid, which forms, with a portion of oxide of iron, a fusible silicate which constitutes the slag.

When the operation is completed, the fused iron is run out into a cistern of cold water, in order that it may be suddenly cooled, and thus rendered brittle. In this way the pig-iron is deprived of the greater part of its impurities, and is converted into *fine metal*, or, as it is also called, *cold-short iron*.

The *fine metal* is now broken up and puddled, in order to complete the purification. The process of puddling consists in fusing the fine metal, in a reverberatory furnace, with a certain amount of oxide, obtained as scoria, in a former operation. The supply of air to the furnace is limited, in order to prevent excessive oxidation of the metal. The mass is well-stirred during the process, so that each portion may be subjected to purification.

As the operation proceeds, the metal, which is at first pretty liquid, becomes pasty, at the same time evolving bubbles of carbonic oxide; when the workman judges that the process is completed, he collects all the particles of metal with his stirrer, and forms them into masses, which are called *puddler's balls*, or *lumps*; these are hammered (or *surgéés*), and subsequently rolled, in order to free them from slag. The bars thus obtained are laid in bundles, raised to a welding heat in another furnace, and welded together, which at once improves their strength and texture. They are then considered marketable bar-iron.

CAST-IRON.

Cast-iron contains, besides iron, carbon, silicon, phosphorus, and traces of manganese;¹ its properties differ according to the quantity of each of these substances.

There are three varieties of cast-iron, known as *black*, *gray*, and *white cast-iron*.

Mottled cast-iron is a mixture of gray and white iron. The black variety is the most unequal in texture, the most fusible, and least cohesive of these. Its color is due to the presence of graphite, formed during the manufacture. When dissolved in acids, it evolves hydrogen of a fetid odor, and leaves a residue of graphite. It is always formed when a considerable excess of carbon is employed in the reduction of the ore, and is much prized for casting.

According to Berthier's analysis, black iron contains generally from 3 to 3.5 per cent. of carbon, from 0.07 to 0.5 per cent. of silicon, and some manganese.

Gray cast-iron is granular in structure, and of sp. gr. between 6.79 and 7.05; when this variety is treated with acids, it leaves a residue of graphite, which is smaller in quantity than that obtained from black iron. Gray iron is more easily oxidized by exposure to air than the white iron, from its superior porosity. This variety contains more phosphorus than the others, which renders it brittle, but, at the same time, more fusible and fit for casting.

It appears to contain from 2 to 3 per cent. of carbon, rather less silicon, from 0.5 to 1 per cent. of phosphorus, and traces of manganese.

Gray cast-iron is the ordinary product of a good operation by the English method. It is used for artillery.

White cast-iron is generally produced when a deficient supply of carbon is employed in the reduction of the ore, or when the ores contain a considerable quantity of manganese.

White cast-iron has a fine metallic lustre and a silvery-white color; its density varies between 7.4 and 7.8; it is exceedingly hard and brittle. White iron fuses more readily than gray iron, but the fused mass is pasty, not liquid.

It would appear that the carbon is contained in a different form of combination in white iron, for it leaves no carbonaceous residue when dissolved in acids.

White cast-iron contains from 2 to 2.5 per cent. of carbon, about 0.5 per cent. of silicon, 0.2 to 0.3 per cent. of phosphorus, and about 2 per cent. of manganese.

Gray cast-iron may be converted into white iron by sudden cooling, or, inversely, the white variety into gray iron, by a high temperature and gradual cooling.²

Bar-iron (wrought-iron) has a bluish-gray color, is very malleable and ductile, and possesses, in most respects, the properties of pure iron. The carbon in bar-iron may amount to 0.25 per cent. without injury to the properties of the metal. Iron containing 2 per cent. of carbon is no longer fit for forging.

It will be inferred, from what has been already stated, that the quality of bar-iron is much injured by the presence, even in small quantities, of phosphorus and sulphur; the latter, especially, exerts an injurious influence upon the metal. The presence of arsenic is also attended with great inconvenience; 0.0005 of phosphorus will render bar-iron unfit for working, an effect which is produced by even 0.0001 of sulphur.

The structure of bar-iron is granular, and the finer the grain, the better, in general, the quality of the iron; when hammered, it becomes fibrous, but re-

¹ Only the principal impurities are here enumerated; traces of other metals are also contained in cast-iron; e. g. cobalt, chromium, calcium, potassium, and sodium.

² This variety (white iron) is only employed for coarse castings, never for machinery.

sumes its granular structure if heated and cooled suddenly. When a bar of fibrous iron is exposed to frequent vibrations, it often assumes a crystalline structure; this is observed in iron railroads, and similar works, and sometimes induces a dangerous brittleness in the metal. A bar of iron also becomes crystalline if it be repeatedly heated and allowed to cool.

The specific gravity of hammered bar-iron is 7.9.

In welding bars of iron together, it is of course necessary that their surfaces should be free from oxide; this is generally insured by sprinkling them with sand, which combines with the oxide to form a fusible silicate.

The purest kind of commercial iron is found in piano-wire, since the metal could not be drawn out into fine wire unless it were nearly pure.

STEEL.

Steel contains more carbon than bar-iron, but less than cast-iron; the amount of this element never exceeding 1 per cent. Steel also contains small quantities of phosphorus and silicon. A specimen of the best English steel was found by Gay-Lussac to contain—

Carbon	0.62
Silicon	0.03
Phosphorus	0.03
Iron	99.32
	<hr/>
	100.00

Small quantities of manganese are also found in most varieties of steel.

Steel (*natural steel*) is sometimes obtained by partially refining the pig-iron until it contains only the proper amount of carbon; the steel thus obtained, however, is chiefly used for agricultural instruments. Pig-iron containing manganese is found to answer best for this purpose. Steel, however, is most commonly made by a process termed *cementation*, in which bar-iron is arranged in alternate layers with charcoal-powder, in a closed chest of refractory clay, which is exposed to a high temperature for several hours. In this process, it is probable that the carbon first combines with the oxygen of the air, inclosed in the chest, to form carbonic oxide, which then yields up part of its carbon to the iron, and is converted into carbonic acid, from which carbonic oxide is again formed by the action of the heated charcoal. The result of this operation is termed *blistered steel*, from the appearance of its surface.

In order to convert blistered steel into *shear-steel*, several bars are welded together, and the bar thus obtained again divided and welded, until steel of the requisite quality is obtained. The cutting and welding are designed to improve the texture of the metal, and to render it homogeneous.

Cast-steel, which is the best variety, is obtained by fusing blistered steel, casting it into ingots, and bringing these under the hammer.

Properties of Steel.—Steel differs much from iron; it is much harder, of finer grain, and more sonorous. The specific gravity of steel is generally 7.74.

The most important and useful property of steel, is that of acquiring very great hardness when heated and afterwards suddenly cooled by immersion in water. The degree of hardness thus acquired depends upon the temperature to which the steel has been raised. For most purposes the steel is too much hardened by this process, and it then becomes necessary to temper the articles by exposing them to a moderate heat in an annealing-furnace. The necessary tempering heat varies for different articles, and is recognized by the workman from the color which the steel assumes, in consequence of the formation of a thin film of oxide upon its surface.

Thus, at 430° F. (221° C.), the surface assumes a yellow color, and at this temperature pen-knives and razors are sufficiently tempered; at 490° F. (254° C.), a brown color appears, showing that scissors, &c., are annealed; again, the temperature for watch-springs and swords is about 550° F. (288° C.), indicated by a bright blue color.¹

It appears that hardened steel contains carbon in a state of combination different from that in which it exists before hardening, for it then leaves a considerable residue of carbon when treated with acids; whereas, in the case of hardened steel, all the carbon is evolved in combination with hydrogen, suggesting that it had been in more intimate combination with the iron.

Steel which has taken up too much carbon in the process of cementation, is sometimes reduced in hardness by imbedding it in finely powdered sesquioxide of iron or manganese, and exposing it to a high temperature, when a portion of the carbon is oxidized at the expense of the metallic oxides.²

Instruments of comparatively soft metal are sometimes hardened externally by exposing them to partial cementation; the metal is then called *case-hardened*.

Steel may readily be distinguished from malleable iron, by moistening with dilute nitric acid, and observing the color of the resulting stain; that produced upon steel is dark-gray, while that obtained upon malleable iron is green.

A method of analyzing iron-ores, which should comprehend every constituent which they might contain, would be exceedingly complicated, difficult of execution, and of little practical value. For nearly all technical purposes it is sufficient to ascertain the quantities of iron, of clay, sand, water, carbonic acid, lime and magnesia contained in the ore.

The determination of the iron may be effected either by the dry or the wet process.

The dry assay of iron-ores consists in fusing 200 or 300 grs. of the ore, in a crucible lined with charcoal, with a flux consisting of chalk or clay (free from iron) according to the nature of the gangue. The crucible is exposed to a very high temperature for about an hour and a half, allowed to cool, and the button or buttons of iron freed from adhering slag, and their weight determined. The button may afterwards be broken by a sharp blow, and the fracture examined; if the metal present a grayish or mottled appearance, and be slightly flattened under the hammer, it may be considered as of good quality; but should it be very brittle, and its fracture white and crystalline, the ore cannot be regarded as yielding an iron of the best description.

For the method of analyzing iron-ores in the wet way, see Quantitative Analysis, Special Methods.

MANGANESE.

Sym. Mn. Eq. 27.6. Sp. Gr. 7.05.

§ 234. This metal is found in considerable abundance in nature, in combination with oxygen. It generally accompanies iron.

Preparation.—Manganese is prepared by reducing its oxide with carbon at a high temperature. The carbonate of (protoxide of) manganese is calcined in a closed crucible, when its carbonic acid is expelled; the residual oxide is then

¹ Faraday and Stodart have observed that the hardness of steel may be much increased by alloying it with a very small quantity of either silver, platinum, iridium, or rhodium.

² Cast-iron is sometimes submitted to an analogous process, when it is desirable to transform castings into malleable metal.

mixed with oil and fine charcoal to a paste, which is moulded into pellets and introduced into a crucible lined with charcoal; this latter is heated for two or three hours in a wind-furnace, after which a button of metal will be found at the bottom of the crucible. This button, however, bears the same relation to pure manganese as cast-iron does to the pure metal; in order to separate the carbon from it, it must be again fused, with a little carbonate of manganese and vitrified borax.

Properties.—Manganese is an iron-gray, feebly lustrous, hard, brittle metal. It is as difficult of fusion as iron. When exposed to air (especially if moist) it is soon oxidized, and should therefore be kept in sealed tubes, or under coal-naphtha.

It has but little action upon water at the ordinary temperature, but decomposes it rapidly at the boiling-point, or in presence of an acid.

MANGANESE AND OXYGEN.

(Prot.) oxide of manganese	MnO.
Sesquioxide "	Mn ₂ O ₃ .
Binoxide or Peroxide "	MnO ₂ .
Manganic acid	MnO ₃ .
Permanganic acid	Mn ₂ O ₇ .

Some intermediate oxides of manganese also exist.

OXIDE, OR PROTOXIDE, OF MANGANESE.

MnO. Eq. 35.6.

§ 235. The anhydrous oxide is prepared by heating the carbonate in a bulb-tube, through which a stream of dry hydrogen is passing; the latter only serves to exclude the air, and exerts no reducing action.

It has a green color, and is not decomposed by heat. When exposed to air, it soon absorbs oxygen, and becomes brown; it is less liable to oxidize after powerful ignition; when heated in air or oxygen, it is converted into an oxide having the composition Mn₂O₃ (*red oxide*).

Hydrated Oxide of Manganese is precipitated when a protosalt of this metal is decomposed by an alkali; it is a white precipitate, which rapidly absorbs oxygen from the air, becoming brown.

The oxide of manganese is a pretty powerful base; it dissolves in acids, and forms some important salts.

Solutions of the neutral salts of this oxide do not change the color of test-papers.

SULPHATE OF OXIDE OF MANGANESE. SULPHATE OF MANGANESE.

MnO SO₄.

Preparation.—To prepare this salt, powdered binoxide of manganese is heated with concentrated sulphuric acid:—



The pure mass is heated with water, the solution filtered, and digested with an excess of carbonate of manganese, which precipitates the sesquioxide of iron; the clear liquid, when evaporated, yields crystals of the sulphate.

Sulphate of manganese is also prepared by heating to dull redness a mixture of equal weights of sulphate of iron and binoxide of manganese; the salt is extracted from the mass by water, and sesquioxide of iron is left, together with the excess of binoxide of manganese.

Properties.—Sulphate of manganese forms large transparent crystals, which have a pink color, of varying intensity. The shape and composition of these crystals differ with the temperature at which they are deposited.

When a hot concentrated solution of sulphate of manganese is allowed to cool, the crystals which are deposited between 68° and 86° F. (20° and 30° C.), have the formula $\text{MnO.SO}_3.\text{HO}+3\text{Aq}$, and are isomorphous with the corresponding iron-salt. Those which are deposited between 43° and 68° F. (6° and 20° C), are composed of $\text{MnO.SO}_3.\text{HO}+4\text{Aq}$; they have the same form as the crystals of sulphate of copper. Below 43° F. (6° C.) the formula of the crystals is $\text{MnO.SO}_3.\text{HO}+6\text{Aq}$, and their form is the same as that of the sulphate of iron with 7 equivalents of water.

The ordinary crystals of this salt are those containing 4 equivalents of water. They are readily soluble in water, but insoluble in alcohol, which abstracts part of their water of crystallization. If these crystals are dried at a temperature of about 400° F. (204° C.), they lose their water of crystallization, leaving the salt $\text{MnO.SO}_3.\text{HO}$, which is also deposited when an aqueous solution is boiled for some time.¹

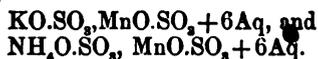
The perfectly anhydrous salt may be obtained by moderately igniting the crystals. It readily absorbs 3 equivalents of water from the air.

When heated to redness, sulphate of manganese is decomposed, sulphuric and sulphurous acids are evolved, and the red oxide of manganese left:—



Sulphate of manganese is used in dyeing and calico-printing; occasionally, also, in medicine.

The equivalent of constitutional water in sulphate of manganese may be replaced by the sulphates of potassa and ammonia, *double salts* being formed which are represented by



A *double sulphate of manganese and alumina*, of the formula



is found in colorless fibrous crystals, in Algoa Bay (Africa); it is soluble in water. This salt is evidently *manganese-alumina-alum*.

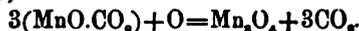
Phosphate of Manganese, 2MnO.HO.PO_3 , occurs in the mineral kingdom.

CARBONATE OF MANGANESE, MnO.CO_3 .

This salt is also found in nature, sometimes in rose-colored rhombohedra (*manganese spar*). It is generally associated with the carbonates of iron and lime, with which it is isomorphous.

Carbonate of manganese may be prepared by precipitating solution of the sulphate with carbonate of soda, and washing the precipitate till free from sulphuric acid.

It has a pinkish-white color, and when heated in air, is easily converted into the red oxide (Mn_2O_3);



This carbonate is insoluble in water, but dissolves in carbonic acid water.

It is employed for the preparation of other compounds of manganese.

Silicates of Manganese are found in nature. The silicate of the formula $3\text{MnO.SiO}_2+3\text{Aq}$, is black, and may be decomposed by acids, while another, the composition of which is 3MnO.2SiO_2 , resists the action of acids.

¹ Other hydrated salts have been obtained, of the formulae $\text{MnO.SO}_3.\text{HO}+\text{Aq}$, and $\text{MnO.SO}_3.\text{HO}+2\text{Aq}$.

SESQUIOXIDE OF MANGANESE.



§ 236. This oxide constitutes the minerals *braunite* and *manganite*; the former is the anhydrous sesquioxide, whilst the latter contains $\text{Mn}_2\text{O}_3 \cdot \text{HO}$. The sesquioxide is often associated with the binoxide.

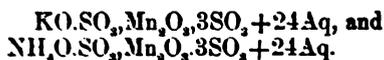
It is a brownish-black substance, which possesses feeble basic properties; at a low temperature it forms sesquichloride, when dissolved in hydrochloric acid, but this solution evolves chlorine when heated, the (proto-) chloride of manganese being formed—



The *hydrated sesquioxide of manganese* is formed when the hydrated (prot-) oxide is exposed to air.

The salts of sesquioxide of manganese are not very well known; they are unstable, easily evolving oxygen, and being converted into salts of the (prot-) oxide.

The *Sulphate of Sesquioxide of Manganese*, $\text{Mn}_2\text{O}_3 \cdot 3\text{SO}_3$, is obtained by dissolving the sesquioxide in sulphuric acid, at a very gentle heat; it crystallizes with difficulty; the solution has a red color, and is instantly decomposed by heat, or by deoxidizing agents. By adding sulphate of potassa, or of ammonia, to the solution, fine crystals of *manganese-alums* may be obtained, the formulæ of which are:—



RED OXIDE OF MANGANESE, OR PROTOSSESQUIOXIDE OF MANGANESE,



This oxide occurs in nature, and is known by the name of *Hausmanite*.

It is the most stable (with respect to heat) of all the oxides of manganese, and is always formed when they are heated in air. This oxide constitutes the residue left in the retort after the preparation of oxygen from binoxide of manganese, and may be employed for the preparation of chlorine from hydrochloric acid.

With acids, it behaves like a combination of MnO with Mn_2O_3 .

Manganese is always determined in the form of the red oxide.

BINOXIDE, OR PEROXIDE, OF MANGANESE.



This most important of the oxides of manganese is found naturally in abundance, sometimes in prismatic crystals, sometimes in radiated crystalline masses. When pure it is called by mineralogists *pyrolusite*; it is, however, generally associated with magnetite, hausmanite, sesquioxide of iron, carbonates of lime and barytes. It is sometimes found in combination with barite, as *psilomelane*.

The red oxide may be purified by washing with dilute nitric acid, to which it is insoluble.

Manganous oxide may be obtained as a black precipitate by adding a solution of hypochlorite (chloride) of lime to one of sulphate of manganese.

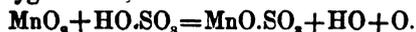
The *proto-oxide* of manganese has a steel-gray color, and may be purified by washing with black. When heated, it is decomposed as before into sesquioxide and red oxide of manganese.

Binoxide or *peroxide* of manganese has characters are neither basic nor acidic. It is a powerful oxidizing agent, and is capable of converting sulphurous acid into sulphuric acid, according to the temperature.

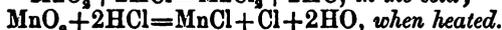
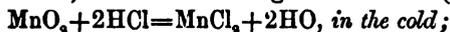
When in contact with oxalic acid, it yields *oxalate of manganese* and carbonic acid :—



A mixture of dilute sulphuric acid with this oxide is frequently used as an oxidizing agent, especially in organic chemistry ; it will be remembered that such a mixture evolves oxygen when heated :—



When precipitated hydrate of binoxide of manganese is treated with hydrochloric acid in the cold, it entirely dissolves, forming a dark brown liquid, which appears to contain bichloride of manganese, MnCl_2 , and becomes colorless when heated, evolving chlorine, the bichloride being converted into (proto-) chloride :—



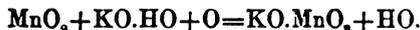
The natural binoxide of manganese is decomposed, though less readily, in the same way, and this principle is applied in the preparation of chlorine.

Hydrobromic, hydriodic, and probably also hydrofluoric acid, evolve their salt-radicals when heated with binoxide of manganese.

When heated in a closed vessel with caustic potassa, the binoxide is decomposed into sesquioxide and manganic acid :—



If air be allowed access, all the manganese is converted into manganate of potassa :—



Binoxide of manganese dissolves in fused glass, to which it imparts a fine purple-violet color, which is often observed in window-glass.

Uses.—Binoxide of manganese is largely employed for preparing chlorine, and is thus of great importance to the manufacturer of bleaching-powder. Moreover, glass-makers employ considerable quantities to decolorize their glass, either by peroxidizing any (prot-) oxide of iron which may be present, or by oxidizing any carbonaceous matters. It is also used in coloring glass.

The calico-printer makes use of it for obtaining a black or brown color, for which purpose the hydrated binoxide is precipitated in the fabric by the action of chloride of lime upon the sulphate of manganese. We have encountered many examples of the use of this oxide in the laboratory.

MANGANIC ACID, MnO_3 .

§ 237. This acid has not yet been isolated, in consequence of its instability; but it is well known in its combinations with bases.

MANGANATE OF POTASSA, CHAMELEON MINERAL, KO.MnO_4 .

This salt is always formed when a compound of manganese is fused with potassa or its carbonate in presence of an oxidizing agent.

Preparation.—The best method of preparing it consists in fusing an intimate mixture of binoxide of manganese and hydrate of potassa in a current of oxygen. One part of binoxide in impalpable powder is mixed with one part of hydrate of potassa dissolved in a little water; the paste is dried, introduced into a tube of hard glass, and heated to dull redness for some time in a current of oxygen. When the mass is afterwards digested with a little cold water, it gives a dark emerald-green solution, which must be filtered through asbestos, and carefully evaporated *in vacuo* over oil of vitriol; fine green crystals are thus obtained, which are freed from mother-liquor by draining on a porous tile.¹

¹ Another process for obtaining this salt in larger quantity, though in an impure state, will be described in the method for preparing permanganate of potassa.

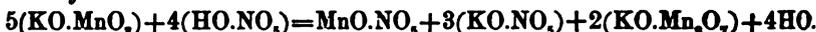
Properties.—These crystals dissolve without alteration in solution of potassa, but they are decomposed by water, yielding a red solution of *permanganate of potassa*, and a brown precipitate of the hydrated binoxide of manganese:—



A similar decomposition may be effected by adding a large quantity of water to the alkaline solution, especially if the temperature be raised. The changes of color thus produced have caused the name *chameleon mineral* to be bestowed upon the mass obtained by fusing the binoxide of manganese with alkalis and oxidizing agents.

Solution of manganate of potassa is easily decomposed by reducing agents; contact with organic matters speedily changes it, so that it must not be filtered through paper; in these cases, the manganic acid is converted generally into sesquioxide of manganese.

The solution of manganate of potassa is easily converted into the permanganate by acids:—



Manganate of potassa possesses a very high coloring power; a very small quantity of this salt will color a large amount of liquid; hence its production is frequently employed as an indication of the presence of manganese.

The *Manganate of Soda* much resembles the potassa-salt, the other manganates are insoluble.

Manganic acid is isomorphous with sulphuric, selenic, and chromic acids, their salts having the same crystalline form.

PERMANGANIC ACID, HYPERMANGANIC ACID, Mn_2O_7 .

This acid is prepared by decomposing permanganate of baryta with sulphuric acid (dilute), decanting the clear liquid, and evaporating *in vacuo* over oil of vitriol, at as low a temperature as possible.

It forms a brown crystalline mass, which is very readily soluble in water.

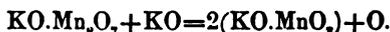
Permanganic acid is also very unstable. It is decomposed at 80° or 90° F. into oxygen and binoxide of manganese; organic matters, ammonia, and reducing agents generally, decompose it with facility.

PERMANGANATE OF POTASSA, $\text{KO.Mn}_2\text{O}_7$.

Preparation.—In order to prepare this salt in a pure state, 4 parts of finely-powdered binoxide of manganese are intimately mixed with 3½ parts of chlorate of potassa; to this mixture are added 5 parts of hydrate of potassa, dissolved in a very small quantity of water; the pasty mass is dried, and fused for an hour or so in an earthen crucible. When cold, it is extracted with a considerable quantity of water, the solution filtered through asbestos, and evaporated at as low a temperature as possible, when fine crystals of the permanganate are deposited.

Properties.—These crystals have a dark-red color; they are soluble in about 16 parts of cold water. Permanganate of potassa is a powerful oxidizing agent; it is deoxidized under the same circumstances as the manganate, and with similar results; even the organic matters floating in the air are capable of decomposing this salt.

If a solution of permanganate of potassa be mixed with an excess of caustic potassa, its color changes to green, manganate of potassa being formed, and oxygen liberated:—



Uses.—Permanganate of potassa is employed for the detection of sulphurous acid in officinal hydrochloric acid, and of the inferior oxides of nitrogen in nitric acid, since its very intense red color is destroyed with the greatest ease by

reducing agents. It also receives application in the determination of iron, in quantitative analysis.

Permanganate of Baryta, which serves for the preparation of the acid, may be obtained by igniting binoxide of manganese with nitrate of baryta, or by decomposing a hot solution of permanganate of silver with chloride of barium, when chloride of silver is precipitated, and permanganate of baryta remains in solution.

The *permanganate of silver* may be prepared by adding nitrate of silver to a hot concentrated solution of permanganate of potassa; the silver-salt crystallizes out on cooling.

CHLORIDE, OR PROTOCHLORIDE, OF MANGANESE, $MnCl$.

§ 238. This salt is prepared from the residues left after the preparation of chlorine from hydrochloric acid, and binoxide of manganese. The solution is evaporated to dryness, the residue dissolved in a little water, and the chloride of manganese allowed to crystallize out; the crystals are redissolved in water, the solution boiled with a little carbonate of manganese to precipitate the sesquioxide of iron, filtered, and again evaporated to crystallization.

The chloride crystallizes in pink, four-sided tables, of the formula $MnCl + 6Aq$. They deliquesce in moist air. When heated, these become anhydrous, and undergo the igneous fusion; if the fused salt be ignited in air, chlorine is expelled, and the manganese oxidized. Anhydrous chloride of manganese dissolves in 2 parts of water at $144^{\circ} F.$ ($62^{\circ} C.$), which is its point of greatest solubility. It also dissolves in alcohol. This chloride is used in dyeing. It is also employed, occasionally, for the purification of gas, since it readily decomposes the sulphide of ammonium and carbonate of ammonia found among the products of the distillation of coal.

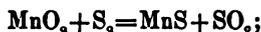
Chloride of manganese forms a crystallizable *double-salt* with *chloride of ammonium*.

The *Sesquichloride of Manganese* (Mn_2Cl_3) is only known in solution, which has a deep-brownish color, and is decomposed by heat, evolving chlorine; it is obtained when hydrated sesquioxide of manganese is dissolved in hydrochloric acid.

The same remarks apply to the *bichloride*.

SULPHIDE OF MANGANESE, MnS .

This compound is found native in compact brilliant masses of a black color, becoming green when powdered; it is called *manganese-blende*. The anhydrous sulphide may be prepared by heating to redness a mixture of binoxide of manganese and sulphur:—



it is thus obtained as a dark green powder.

When heated in air, sulphide of manganese is converted into sulphurous acid, and protosulphide of manganese. It is decomposed by acids, especially nitric.

Hydrated sulphide of manganese is obtained as a flesh-colored precipitate, when a solution of a salt of manganese is decomposed by an alkaline sulphide; when exposed to air, it soon becomes brown, being partially converted into one of the higher oxides of manganese. If heated out of contact with air, it loses water, and is converted into the dark green anhydrous sulphide. The hydrate is dissolved by sulphuric, hydrochloric, and nitric acids.

An *oxysulphide of manganese* is formed when hydrogen is passed over sulphate of manganese at a red heat; it has a green color, and burns when heated in air, being converted into sulphurous acid and proto-sesquioxide of manganese. It dissolves in acids, with evolution of hydro-sulphuric acid.

Compounds of sulphide of manganese with the sulphides of potassium and sodium, having the composition $KS.3MnS$, and $NaS.3MnS$, are obtained by

heating a mixture of dry sulphate of manganese with $\frac{1}{2}$ part of charcoal, 3 parts of carbonate of potassa or soda, and an excess of sulphur. When the fused mass is treated with water, the double sulphide is left as a dark-red, crystalline powder, which is easily oxidized when exposed to air, and is readily acted upon by acids.

ZINC.

Sym. Zn. Eq. 32.6.

§ 239. This metal is pretty abundant in nature, and is important from its numerous applications. We shall therefore devote a section to the technical history of zinc, after we have become acquainted with its chemical properties.

Preparation.—The zinc of commerce contains about 1 per cent. of impurities, consisting of lead, iron, tin, carbon, copper, cadmium, and arsenic. In order to purify it, it is subjected to distillation in an earthen crucible, furnished with an earthen tube which passes through the bottom of the crucible and extends nearly to the top; this tube projects downwards through the bars of the furnace, and nearly touches the surface of water in a reservoir situated in the ash-pit. The crucible is half filled with zinc, and strongly heated, when the metal condenses in the water. The distilled metal still contains a little lead, cadmium, and arsenic; it is freed from the latter by fusing with about $\frac{1}{2}$ its weight of nitre, which converts it into arseniate of potassa; the mass is treated with water, and the metal dissolved in dilute sulphuric acid, which leaves the lead as insoluble sulphate; a current of sulphuretted hydrogen is now passed through the highly diluted solution, to remove the cadmium as sulphide; the filtered liquid contains only sulphate of zinc, which may be precipitated by carbonate of soda, and reduced by charcoal.

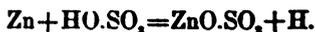
Properties.—Zinc is a bluish-white, lustrous metal, with a lamellar, crystalline structure; it is somewhat brittle at the ordinary temperature, but becomes malleable at a little above 212° F. (100° C.), and may be rolled into plates, or drawn out into fine wires. At about 400° F. (204° C.), it again becomes brittle, and may be reduced to powder.

This metal fuses below a red heat, and boils at a white heat, when it may be distilled unchanged. If fused zinc be allowed to cool gradually, it crystallizes in prisms with hexagonal bases. If it be poured into water, it is divided into small irregular masses, or *granulated*. The sp. gr. of cast-zinc is 6.8; that of rolled zinc, 7.2. It possesses very little tenacity; a wire of $\frac{1}{16}$ inch in diameter will only support 26 lbs.

Zinc is unaltered by exposure to dry air, but in moist air it soon becomes covered with a thin film of oxide of zinc, which absorbs a little carbonic acid from the air. When heated in air a little above its fusing-point, it takes fire, and burns with a greenish-white, highly luminous flame, producing a thick, white smoke of oxide of zinc (*philosopher's wool*).

Water free from air and carbonic acid has no action upon zinc, but common water converts a portion of the metal into carbonate of zinc, since it is oxidized either by the air in the water, or even at the expense of the latter, hydrogen being disengaged. When vapor of water is passed over zinc at an elevated temperature, oxide of zinc is formed, and hydrogen evolved; the decomposition of the water commences even at 212° F. (100° C.)

Zinc decomposes water very readily at the ordinary temperature, in presence of acids; thus, with sulphuric acid:—



If pure zinc be immersed in dilute sulphuric acid, it becomes covered with a number of hydrogen bubbles, which protect it from further action, but if a negative plate be provided, from which the bubbles may be disengaged, the action is continuous; in ordinary zinc, the impurities supply a series of such negative plates.

The readiness with which weak acids act upon zinc warns us against employing this metal largely for culinary purposes, since its salts are poisonous.

The hydrogen acids readily dissolve zinc, concentrated sulphuric acid in the cold scarcely affects it. Solutions of potassa, soda, and even of ammonia, are capable of dissolving zinc, with evolution of hydrogen and formation of compounds of oxide of zinc with the alkalies.

Zinc is capable of precipitating a great many metals from their solutions; copper, tin, antimony, and silver may serve as examples.

ZINC AND OXYGEN.

Suboxide of zinc	Zn ₂ O.
(Prot-) oxide "	ZnO.
Peroxide "	ZnO ₂ .

SUBOXIDE OF ZINC, Zn₂O.

§ 240. The existence of this oxide is not very certain, since it has never been obtained in a pure state; it is said to be formed when zinc tarnishes in moist air. When oxalate of zinc is carefully heated in a close vessel, it leaves a dark gray substance, which is supposed to be the suboxide; it is decomposed by acids into oxide of zinc and metal.

OXIDE, OR PROTOXIDE OF ZINC.

ZnO. *Eq.* 40.6.

This oxide occurs in nature as *red zinc-ore*.

Anhydrous oxide of zinc is formed when zinc is burnt in air, or heated in an atmosphere of steam; in the latter case it is crystalline.¹

Preparation.—It is best prepared by calcining the precipitate produced by mixing solutions of sesquicarbonate of ammonia and sulphate of zinc.

On the large scale it is made by vaporizing zinc in earthen cylinders through which a current of air is passed.

Properties.—It forms a light white powder which becomes yellow when heated, and white again on cooling. Oxide of zinc is perfectly fixed and cannot be decomposed by heat. When exposed to air, it becomes partly converted into carbonate. It is insoluble in water, but dissolves easily in acids; its salts have the same crystalline form as those of magnesia and oxide of iron, with which it is isomorphous. Even those salts which are neutral in constitution, are found to have an acid reaction.

Oxide of zinc is not easily soluble in solutions of potassa and soda, but if it be fused with these in a silver crucible, it forms compounds soluble in water, in which the oxide of zinc appears to play the part of an acid.

This oxide has been used, of late years, as a substitute for white-lead (carbonate of lead) as a pigment (*zinc-white*); it possesses the advantages of not affecting the health of the painters, and of being unaltered by sulphuretted hydrogen, which blackens lead-paint.

Oxide of zinc is also used in medicine.

¹ Rectangular four-sided prisms of this oxide have been formed accidentally in the distillation of zinc.

Hydrated Oxide of Zinc ($ZnO.HO$) may be prepared by adding solution of potassa to solution of sulphate of zinc, avoiding an excess; it forms a white precipitate which should be dried by simple exposure. When freshly precipitated it is easily soluble in potassa, soda, or ammonia, but after drying, not so readily.

Prismatic crystals of this hydrate may be obtained by introducing a voltaic couple of zinc and iron into a solution of potassa or ammonia.

§ 241. NITRATE OF ZINC ($ZnO.NO_3$) prepared by dissolving zinc in dilute nitric acid, crystallizes in four-sided prisms, containing 6 eqs. water. It is deliquescent, and very soluble in water and alcohol.

SULPHATE OF OXIDE OF ZINC. SULPHATE OF ZINC. WHITE VITRIOL.



Preparation.—This salt is obtained on the large scale by roasting native sulphide of zinc (*blende*), extracting with water, and evaporating the solution to the crystallizing point; for convenience of transport, the salt is generally fused in its water of crystallization, and sent into commerce in white masses. These are generally contaminated with the sulphates of magnesia, iron, and copper.

To prepare pure sulphate of zinc, commercial zinc is dissolved in dilute sulphuric acid, and a little chlorine added to peroxidize any iron which may be present; the solution is then heated with carbonate of zinc, which precipitates the sesquioxide of iron, filtered, and evaporated to crystallization.

Pure sulphate of zinc, when dissolved in water and boiled with a little nitric acid, should give no brown precipitate, with excess of ammonia (indicating iron), and no blue color (due to copper).

Properties.—The formula of the ordinary crystals of this salt is $ZnO.SO_4.HO+6Aq$, but salts containing less water of crystallization have been obtained.

A sulphate of the formula $ZnO.SO_4.HO+4Aq$ may be obtained by boiling the ordinary crystals for some time with alcohol; another salt, containing only 2 eqs. of water of crystallization, is precipitated when concentrated sulphuric acid is added to a strong solution of the sulphate. The ordinary salt forms prismatic crystals, which lose their 6 eqs. of water of crystallization at $212^\circ F.$ ($100^\circ C.$), undergoing the aqueous fusion; at a higher temperature, the water of constitution is expelled, and if the heat be still continued, sulphurous acid and oxygen pass off, and a basic sulphate is left, which is decomposed at a red heat into sulphurous acid, oxygen, and oxide of zinc.

The crystals are soluble in about $2\frac{1}{2}$ parts of water at the ordinary temperature, and insoluble in alcohol.

The solution of sulphate of zinc has an acid reaction to test-papers.

Uses.—Sulphate of zinc is employed to induce vomiting; it is poisonous in moderately large quantities. Sulphate of zinc is used by dyers.

Several basic sulphates of zinc are said to exist.

Sulphate of zinc is capable of combining directly with ammonia, forming definite compounds, which are easily decomposed by heat.

This salt forms double sulphates with those of potassa, ammonia, magnesia, and protoxide of iron. The potassa and ammonia salts have the formulæ $Zn(O.SO_4).K(O.SO_4)+7Aq.$ and $Zn(O.SO_4).NH_4O.SO_4+7Aq.$

CARBONATE OF ZINC. $ZnO.CO_2$

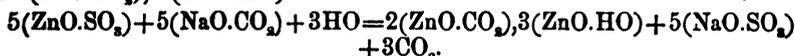
This salt occurs in nature as *malachite*, which is sometimes found in amorphous masses, sometimes in crystals of the same form as those of carbonate of lime. Crystals of this compound have been prepared by exposing to the air solutions of oxide of zinc in potassa and soda.

It may be prepared by a process similar to that described for the preparation of sulphate of zinc, with the use of magnesia, see p. 357.

When heated, carbonate of zinc is easily converted into oxide. It is insoluble in water, but dissolves to a slight extent in solution of carbonic acid. Carbonate of zinc also dissolves in solution of carbonate of ammonia; after a time, the solution deposits crystals of the formula $2(\text{ZnO}.\text{CO}_2).\text{NH}_3$.

Carbonates of potassa and soda form double carbonates with that of oxide of zinc.

The precipitate produced by alkaline carbonates in solutions of zinc-salts is a variable *compound of hydrate and carbonate*, of which the most common formula is $2(\text{ZnO}.\text{CO}_2), 3(\text{ZnO}.\text{HO})$:—



Calamine is the chief ore of zinc; when previously prepared by levigation it is sometimes used in surgery.

The *silicate of zinc* is found in nature, and is sometimes termed *electric calamine (zinc-glance)*.

BINOXIDE OF ZINC, ZnO_2 .

This oxide has been obtained by the action of binoxide of hydrogen upon hydrated oxide of zinc. It is insoluble in water, and is easily decomposed, even at ordinary temperatures, the second equivalent of oxygen being disengaged.

CHLORIDE OF ZINC, ZnCl .

§ 242. The chloride is formed, with combustion, when finely divided zinc is introduced into chlorine.

Preparation.—It may be prepared by dissolving granulated zinc in hydrochloric acid, and evaporating, when it may be obtained in the form of a semisolid hydrated mass, known as *butter of zinc*; if this be further heated, it fuses and becomes anhydrous, when it may be poured upon a slab and allowed to solidify.

Properties.—Chloride of zinc forms white masses, which readily deliquesce when exposed to air; it fuses easily, and may be distilled. This salt is remarkably soluble in water; alcohol also dissolves it, and combines with it to form a crystallizable compound.

When heated strongly in air, chloride of zinc is partly converted into oxide, chlorine being evolved. The hydrated chloride, when strongly heated, evolves hydrochloric acid, and leaves a residue of *oxychloride of zinc*, so that it is better to dry it in a current of hydrochloric acid.

Uses.—The great affinity of chloride of zinc for water often renders it useful in experiments upon organic substances.

Chloride of zinc is also sometimes employed to purify the air from sulphuretted hydrogen, which it converts into sulphide of zinc. Sir W. Burnett's disinfecting fluid is a solution of this salt.

A solution of chloride of zinc is also sometimes employed as an antiseptic for the preservation of subjects for dissection; it does not affect the knives, like corrosive sublimate, which is sometimes used for that purpose.

A bath of fused chloride of zinc is occasionally substituted for an oil-bath in chemical operations.

Three *oxychlorides of zinc* are said to exist, containing respectively 3, 6, and 9 equivalents of oxide, combined with 1 equivalent of chloride. They all contain water.

SULPHIDE OF ZINC. ZnS .

This compound is found in nature, and is termed by mineralogists *blende*. It is met with both crystalline and amorphous; the crystals are derived from a cube. Blende is yellow, or brownish-black, and translucent; it is not easily

attacked by acids. It is usually contaminated with iron, cadmium, lead, copper, arsenic, alumina, silica, magnesia, and fluoride of calcium. When blende is roasted in air, sulphurous acid is evolved, and a mixture of oxide and sulphate of zinc is first produced, which is decomposed by a higher temperature, leaving oxide of zinc only.

Sulphide of zinc may be prepared by the direct combination of its elements, or by heating a mixture of oxide of zinc with flowers of sulphur; it is also formed when the sulphate is heated with charcoal; thus obtained, it is a yellow powder.

Hydrated sulphide of zinc is obtained as a white precipitate by adding an alkaline sulphide to a solution of a zinc-salt; it dissolves readily in hydrochloric or nitric acid.

Sulphide of zinc is capable of combining with the sulphides of the alkali-metals at a high temperature.

When hydrogen is passed over anhydrous sulphate of zinc at a red heat, an *oxysulphide* is obtained, which has the formula $ZnO.ZnS$.

Another oxysulphide, of the formula $ZnO.4ZnS$ occurs in nature in a crystalline state, and has been also obtained in metallurgic processes.

METALLURGY OF ZINC.

§ 243. The only ores from which this metal is extracted are the carbonate, or calamine, and the sulphide, known as *blende or black-jack*; the former is the most abundant ore of zinc.

Calamine is calcined to expel water and carbonic acid, before being reduced.

Blende is first roasted with access of air, by which it is converted into oxide of zinc.

The reduction of the metal is very simple. The ore, prepared as above, is mixed with coal or charcoal, and strongly heated in clay retorts, which vary in construction, but, in England, consists of crucibles furnished with an iron tube, which penetrates to some distance within the crucible, and passes through the bottom; the zinc is converted into vapor which condenses in the tube. The metal thus obtained is fused, and cast into ingots.

The progress of the distillation of the zinc is judged of by the workmen from the flame with which the vapors burn at the mouth of the tube; at the beginning of the operation, the flame has a brownish hue, and the zinc which distills contains much cadmium and arsenic; this stage of the operation is termed the *brown blaze*. When a bluish-white flame appears (the *blue blaze*), due to the combustion of carbonic oxide and vapor of zinc, the metal is obtained in a pretty pure state.

In the continental smelting works, the ores are reduced upon the same principle, but various forms of retorts are employed instead of crucibles.

Zinc is sometimes termed *spelter* in commerce.

The uses of zinc are numerous and important. It serves for gutters and water-pipes, for covering the roofs of houses, for coating iron to preserve it from rust (galvanizing), for preparing zinc-white, and other pigments, and as an ingredient of many useful alloys, as brass, German silver, &c., which will be further noticed in their proper places.

Ores of zinc may be roughly assayed in the dry way, by mixing them (after previous roasting) with charcoal, and if the ore be a silicate, with black flux, and heating rapidly to whiteness, when the zinc is volatilized, and may be determined by loss after burning off the excess of charcoal.

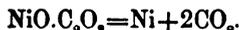
The wet assay is, however, far more satisfactory, but since other metals must be separated before we can determine the zinc, it would be out of place to describe the process here.

NICKEL.

Sym. Ni. *Eq.* 29.6. *Sp. Gr.* 8.5.

§ 244. Nickel, in the combined state, is tolerably abundant in nature; it is generally found, together with iron, in the meteoric stones to which we have before alluded.

Pure nickel may be obtained by strongly igniting the oxalate in a closed crucible.



It is also obtained in a pyrophoric state, by heating oxide of nickel in a current of hydrogen.

Of the method of extracting nickel from its ores we shall speak hereafter.

Properties.—Nickel is a grayish-white metal, with considerable lustre; it is malleable and ductile. This metal, like iron, is attracted by the magnet at ordinary temperatures; it fuses rather more easily than iron, and becomes more fusible when combined with carbon. Nickel is not altered at the ordinary temperature by exposure to moist air, but is oxidized when heated to redness; it burns in oxygen, like iron, and is capable of decomposing water at a red heat.

Nickel dissolves readily in nitric acid, being oxidized and converted into the nitrate; hydrochloric and dilute sulphuric acids act upon it, though less rapidly, hydrogen being evolved.

NICKEL AND OXYGEN.

Oxide of nickel	NiO
Sesquioxide	Ni ₂ O ₃

The existence of a higher oxide than this last has been alleged, but is not certain.

OXIDE, OR PROTOXIDE OF NICKEL.

NiO. *Eq.* 37.6.

§ 245. When nickel is heated to redness in aqueous vapor, it becomes covered with a light olive-green crystalline powder, which consists of anhydrous oxide of nickel. This oxide may also be prepared by heating the hydrate or the basic carbonate of nickel. The oxide thus obtained is said to contain a little sesquioxide of nickel, from which it may be purified by gently heating in a current of hydrogen.¹ It has an ash-gray color, and is not fused or decomposed by heat.

Oxide of nickel is reduced to the metallic state by hydrogen or carbon at an elevated temperature.

This oxide is a pretty powerful base, and forms well-defined salts, which redden litmus-paper.

The *Hydrated Oxide of Nickel*, NiO.HO, is thrown down as an apple-green precipitate, on adding a fixed alkali to a solution of a nickel-salt. It is deposited in a crystalline state from a solution of carbonate of nickel in ammonia.

The hydrate is insoluble in the fixed alkalies, but dissolves with a fine blue color in ammonia. Its water is easily expelled by heat.

NITRATE OF OXIDE OF NICKEL, NITRATE OF NICKEL, NiO.NO₃.—This salt

¹ The crystalline anhydrous oxide has been found in the mineral kingdom, in the form of minute octohedra, which were not attacked by any solvent except boiling sulphuric acid.

forms green crystals, which are deliquescent, and very soluble in water. The crystals contain 6 eqs. of water. It is decomposed by heat, leaving sesquioxide or (prot-) oxide of nickel, according to the temperature employed.

This salt combines with ammonia to form a soluble compound of the formula $\text{NiO} \cdot \text{NO}_3 \cdot 2\text{NH}_3 + \text{Aq}$.

SULPHATE OF OXIDE OF NICKEL, SULPHATE OF NICKEL.

$\text{NiO} \cdot \text{SO}_4$.

The sulphate of nickel may be prepared by dissolving the metal, its oxide, or carbonate, in dilute sulphuric acid, and evaporating the liquid to crystallization.

When the crystals are formed at the ordinary temperature, they are rectangular four-sided prisms, of the formula $\text{NiO} \cdot \text{SO}_4 \cdot \text{HO} + 6\text{Aq}$; but those deposited above 60°F . ($15^\circ.5 \text{C}$.), are octohedra, with the formula $\text{NiO} \cdot \text{SO}_4 \cdot \text{HO} + 5\text{Aq}$. The water of crystallization is expelled at a little above the boiling point, but the water of constitution is not expelled below 527°F . (275°C .)

The crystals have a fine emerald-green color; when exposed to air they lose their water of crystallization, becoming yellow and opaque.

Sulphate of nickel is very soluble in water, but insoluble in alcohol and ether. Its aqueous solution is acid to test-papers.

Anhydrous sulphate of nickel combines with ammoniacal gas, producing a compound of the formula $\text{NiO} \cdot \text{SO}_4 \cdot 3\text{NH}_3$.

When solution of sulphate of nickel is mixed with solution of ammonia, a compound is produced which crystallizes in rectangular prisms of a fine blue color, having the composition $\text{NiO} \cdot \text{SO}_4 \cdot 2\text{NH}_3 + 2\text{Aq}$.

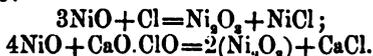
The equivalent of water of constitution in crystallized sulphate of nickel may be replaced by an alkaline sulphate, and, in this way, well-defined crystallizable double-salts are produced. The formula of the *potassa-salt* is $\text{K} \cdot \text{O} \cdot \text{SO}_4 \cdot \text{NiO} \cdot \text{SO}_4 + 6\text{Aq}$.

An insoluble basic sulphate of nickel is obtained when the sulphate is moderately heated, or decomposed by an insufficient quantity of potassa.

No neutral carbonate of nickel has been obtained; the precipitate produced by carbonate of soda in solutions of nickel-salts, has the composition $2\text{NiO} \cdot \text{CO}_2 \cdot 3\text{NiO} \cdot \text{HO} + 2\text{Aq}$.¹

SESQUIOXIDE OR PEROXIDE OF NICKEL, Ni_2O_3 .

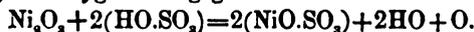
This oxide may be prepared by decomposing the nitrate at a moderate heat. It is also formed when hydrated oxide of nickel comes in contact with chlorine or with a hypochlorite:—



If the solution be decanted from the precipitated sesquioxide of nickel, and boiled, a precipitate of *hydrated sesquioxide*, of the formula $\text{Ni}_2\text{O}_3 \cdot 3\text{HO}$, is obtained.

Sesquioxide of nickel forms a black powder, which evolves oxygen when heated, and is converted into the (prot-) oxide.

It is an indifferent oxide; when heated with sulphuric acid, sulphate of nickel is formed, and oxygen disengaged:—

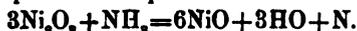


Hydrochloric acid converts it into chloride of nickel, with disengagement of chlorine:—



¹ If a solution of a nickel-salt be precipitated by bicarbonate of potassa, a double-salt of the composition $\text{K} \cdot \text{O} \cdot 2\text{CO}_2 \cdot \text{NiO} \cdot \text{CO}_2 + 10\text{Aq}$ is formed.

Ammonia also decomposes the sesquioxide of nickel :—



The *higher oxide of nickel* mentioned above, the composition of which was said to be doubtful, was obtained by treating the hydrated oxide of nickel with solution of binoxide of hydrogen; it has a dirty-green color, and is very unstable.

CHLORIDE OF NICKEL, NiCl.

§ 246. The anhydrous chloride may be obtained by passing chlorine over nickel at a red heat, or by gently heating the hydrated chloride; in either case it sublimes in fine golden yellow scales, since it is volatile at a moderately high temperature. It dissolves when long boiled with water, yielding a green solution. Chloride of nickel, when heated to redness in hydrogen, yields brilliant metal.

Hydrated chloride of nickel is prepared by dissolving the metal, or its oxide, in hydrochloric acid; it forms yellowish-green crystals, containing nine eqs. of water; they become emerald-green on exposure to air, absorbing moisture. Anhydrous chloride of nickel absorbs ammonia, forming a compound of the composition $\text{NiCl} \cdot 3\text{NH}_3$, which, when heated, leaves metallic nickel.

NICKEL AND SULPHUR.

Subsulphide	Ni ₂ S
(Proto-) sulphide	NiS
Bisulphide	NiS ₂

The *subsulphide* is obtained when sulphate of nickel is decomposed by hydrogen at a red heat.

SULPHIDE, OR PROTOSULPHIDE, OF NICKEL, NiS.

The anhydrous sulphide occurs in nature as *capillary pyrites*. It may be formed by the direct combination of its elements, which takes place energetically at a high temperature. If a mixture of oxide of nickel, carbonate of soda, and sulphur be strongly heated, a lustrous button of sulphide of nickel may be obtained.

Anhydrous sulphide of nickel has a bronze color; it is insoluble in hydrochloric acid, but dissolves in nitric, or in nitrohydrochloric acid.

The *hydrated sulphide* is obtained as a black precipitate, when a nickel-salt is decomposed by an alkaline sulphide. It is slowly oxidized and converted into sulphate when exposed to air.

Hydrated sulphide of nickel dissolves with difficulty in hydrochloric acid, but easily in nitric, or in nitro-hydrochloric acid.

The *bisulphide of nickel* is prepared by calcining an intimate mixture of carbonate of nickel, carbonate of potassa, and sulphur; on treating the mass with water, the bisulphide is left as a steel-gray powder.

METALLURGY OF NICKEL.

§ 247. The chief mineral containing nickel is that termed *copper-nickel* (*Kupfernickel*), so called by the German miners, because they frequently mistook it for an ore of copper; it is an arsenide (arseniuret) of nickel, of the formula NiAs .

Copper-nickel is amorphous, and has a reddish metallic appearance; when roasted in air, it is converted into a basic arseniate of nickel. This mineral is unaffected by hydrochloric acid, but dissolves in nitric acid, or in *aqua regia*. It is often associated with binarsenide of nickel, NiAs_2 .

The *arsenio-sulphide of nickel*, or *gray nickel-ore* (*nickel-glance*), has the formula $\text{NiS} + \text{NiAs}_2$.

It is a similar compound, containing antimony in place of

arsenic. Nickel also occurs in nature as oxide, as sulphide, as arsenite and arseniate, and as silicate (in the mineral *pimelite*).

This metal is always extracted from copper-nickel, or from *speiss*; the latter is a compound of nickel, arsenic, and sulphur, containing small quantities of cobalt, copper, and antimony; it is found at the bottom of the crucibles in which smalt is manufactured (*see p. 373*).

The separation of the nickel and arsenic is attended with very considerable difficulty; numerous methods have been proposed for this purpose, but we must content ourselves with describing only one of them, in order to convey an idea of the principles upon which the separation is based.

The ore is first roasted with access of air, which expels the sulphur, as sulphurous acid, and a great part of the arsenic, as arsenious acid. It is then fused in an earthen crucible with carbonate of potassa and sulphur; the nickel and arsenic are thus converted into sulphides, a quantity of sulphide of potassium being formed at the same time; when the mass is treated with water, the sulphide of potassium enters into solution, and dissolves the sulphide of arsenic, whilst the sulphide of nickel is left, and may either be converted at once into a nickel salt, or may be roasted and transformed into oxide, in which state it may be employed for the preparation of the alloys of nickel, which are used in the arts (*e. g. German silver*).

COBALT.

Sym. Co. Eq. 29.5. Sp. Gr. 8.5.

§ 248. In abundance, cobalt may rank by the side of nickel, to which metal it presents a very striking resemblance in most of its properties; for this reason, the separation of cobalt from nickel, so as to obtain either metal in a state of purity, is a matter of great difficulty, and yet of frequent necessity, since these metals are generally associated in the same ore.

Metallic cobalt may be obtained either by calcining the oxalate, or by reducing the oxide by hydrogen;¹ or, at a very high temperature, by charcoal.

The metal resembles steel in its aspect. Cobalt is fused with great difficulty, but more readily when combined with a little carbon; it is unalterable in moist air, but oxidizes readily at a high temperature. This metal dissolves slowly in hydrochloric and sulphuric acids, but readily in nitric acid.

COBALT AND OXYGEN.

(Prot-) oxide	CoO
Sesquioxide	Co ₂ O ₃

Two intermediate oxides also exist.

OXIDE, OR PROTOXIDE OF COBALT, CoO.

§ 249. The anhydrous oxide is obtained by calcining the hydrate or carbonate, with exclusion of air. It is a nearly black powder, which, when heated in air, absorbs oxygen, and is converted into an oxide of the formula Co₂O₃. Oxide of cobalt colors fluxes dark blue, and this color resists the action of a high temperature, so that it is of great service in the decorative arts.

Oxide of cobalt is soluble in ammonia, giving a fine red liquid.

¹ When reduced at a low temperature, the cobalt is pyrophoric.

When this oxide is fused with potassa, in a silver crucible, it forms a fine blue compound, which is decomposed by water.

Oxide of cobalt combines, at a high temperature, with magnesia, alumina, and oxide of zinc, producing, with the first, a pink compound, and with the last two, blue and green compounds respectively, which are used as colors.

Hydrated Oxide of Cobalt (CoO.HO) is obtained as a pink precipitate, when a solution of a cobalt-salt is treated with excess of potassa; this precipitate is very liable to retain small quantities of potassa. When exposed to air it assumes a dirty green color, from absorption of oxygen.

Oxide of cobalt forms salts with the acids, which are red when hydrated, and become blue on expulsion of their water. The solutions of cobalt-salts are always acid to test-papers. They exhibit a remarkable tendency to form double-compounds with ammonia and ammoniacal salts.¹

NITRATE OF OXIDE OF COBALT, OR NITRATE OF COBALT, CoO.NO_3 .

To prepare the nitrate, the metal or its oxide may be dissolved in nitric acid; it forms small red deliquescent crystals, which are easily decomposed by heat, leaving, unless at a very high temperature, the oxide Co_2O_3 . The crystals contain 6 eqs. water.

A solution of this salt is employed as a reagent.

SULPHATE OF OXIDE OF COBALT, OR SULPHATE OF COBALT, CoO.SO_3 .

This salt occurs in nature; it is obtained by dissolving the oxide in sulphuric acid.

Sulphate of cobalt may be prepared, as a source of other compounds of cobalt, from a Norwegian mineral containing cobalt, iron, arsenic, and sulphur. The finely powdered mineral is roasted in a muffle, with successive additions of powdered charcoal, as long as any arsenical odor is perceptible. The residue is treated with a mixture of sulphuric and (a little) hydrochloric acids, and the sesquioxide of iron precipitated from the solution by boiling with chalk; the solution is then treated with sulphuretted hydrogen, to separate the remainder of the arsenic, &c., filtered, and evaporated to crystallization, when pure sulphate of cobalt is deposited.

At the ordinary temperature it crystallizes in oblique rhombic prisms of the formula $\text{CoO SO}_3.\text{HO}+6\text{Aq}$, but which, at a somewhat higher temperature, have a different form, and contain less water by one equivalent.

The water of constitution may be replaced by alkaline sulphates, forming double salts with 6 eqs. water of crystallization.

The neutral *carbonate of cobalt* is not known; basic carbonates are precipitated when solutions of cobalt-salts are decomposed by alkaline carbonates; the most common of these precipitates has a rose color, and the formula $2(\text{CoO.CO}_2)$, $3(\text{CoO.HO})+\text{Aq}$; it is obtained when a hot solution of a salt of cobalt is precipitated by an alkaline carbonate. If the precipitation be effected in the cold, the formula of the precipitate is $2(\text{CoO.CO}_2)$, $(2\text{CoO.HO})+5\text{Aq}$.²

SESQUIOXIDE OR PEROXIDE OF COBALT, Co_2O_3 .

The anhydrous sesquioxide may be obtained by gently heating the nitrate, or in a crystalline state, by fusing the (prot-) oxide with potassa for a considerable period.

¹ By exposing to the air ammoniacal solutions of cobalt-salts, Fremy has obtained several crystalline salts containing ammonia combined with cobalt in different degrees of oxidation. A nitrate of this description, deposited when ammoniacal nitrate of cobalt is exposed to the air, is decomposed by cold water, with evolution of oxygen.

² If a solution of cobalt is mixed with an excess of bicarbonate of potassa in the cold, a compound of the formula $\text{KO.CO}_2.\text{CoO.CO}_2+10\text{Aq}$ is obtained.

The hydrate, $\text{Co}_2\text{O}_3 \cdot \text{HO}$, is obtained by passing a current of chlorine through water in which hydrated protoxide or carbonate of cobalt is suspended (*see Sesquioxide of Nickel*).

Sesquioxide of cobalt, whether anhydrous or hydrated, is black; when heated, it is converted into the proto-sesquioxide of cobalt, Co_2O_3 . Sesquioxide of cobalt possesses feeble basic properties; it dissolves in dilute acids, yielding brown liquids which evolve oxygen when heated, leaving salts of the (prot-) oxide of cobalt. When this oxide is heated with hydrochloric acid, chlorine is disengaged.¹

Sesquioxide of cobalt is capable of combining with the (prot-) oxide, and of forming certain *proto-sesquioxides*.

It has already been noticed that a black oxide of the formula $\text{Co}_2\text{O}_4 (= \text{CoO} \cdot \text{Co}_2\text{O}_3)$ is obtained when the sesquioxide is decomposed by heat.

When the (prot-) oxide of cobalt, or its carbonate is heated in air, it is converted into Co_2O_3 , or $\text{Co}_2\text{O}_4 (= 4\text{CoO} \cdot \text{Co}_2\text{O}_3)$ according to the temperature.

CHLORIDE OF COBALT, CoCl_2 .

§ 250. This salt may be prepared by dissolving the oxides of cobalt, or the carbonate, in hydrochloric acid; the pink solution yields, on evaporation, rose-colored crystals of the hydrated chloride. If the pink solution be mixed with an excess of acid, it becomes of a blue color, or green if iron or nickel be present. The solution resumes its original red color when largely diluted with water.

When the crystals of hydrated chloride are heated, they lose their water, and evolve hydrochloric acid, oxide of cobalt being left, while a portion of anhydrous chloride sublimes. If only moderately heated, the crystals merely lose their water, becoming blue; this property renders it useful as a sympathetic ink, for letters written with the pink solution are invisible until they are held before the fire, when the chloride loses its water and becomes blue, but resumes its pink color when exposed to air.

Anhydrous chloride of cobalt combines with ammonia, forming the compound $\text{CoCl}_2 \cdot 2\text{NH}_3$.²

The *sesquichloride of cobalt* formed when the sesquioxide is dissolved in hydrochloric acid, is exceedingly unstable.

COBALT AND SULPHUR.

(Proto-) sulphide	CoS .
Sesquisulphide	Co_2S_3 .
Bisulphide	CoS_2 .

¹ Some remarkable conjugate compounds of sesquioxide of cobalt have been examined by Genth. By mixing chloride or sulphate of cobalt with a large quantity of chloride of ammonium, adding ammonia in excess, and acidifying the mixture with hydrochloric acid, after four or five weeks' exposure to air, a solution is obtained which, when boiled, deposits a carmine salt of the formula $\text{Co}_2\text{O}_3 \cdot 3\text{NH}_4\text{Cl}$, which its discoverer regards as the chloride of a new radical, $\text{Co}_2\text{O}_3 \cdot 3\text{NH}_4$, other compounds of which have been obtained by double decomposition.

² By the action of ammonia upon a solution of chloride of cobalt, mixed with chloride of ammonium, Claudet has obtained a red crystalline compound, composed of $2\text{CoCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 4\text{NH}_3$.

At a later period, in investigating the same subject, Rogojski obtained a chloride of the formula $\text{CO}_2\text{Cl}_2 \cdot 3\text{N}_2\text{H}_5$, which is possessed of basic properties.

Fremy has examined the action of hydrochloric acid upon the ammoniacal salts of cobalt; he has obtained a new series of salts, in which part of the oxygen is replaced by chlorine; they have a fine violet color, and are nearly insoluble in water; the chlorine in these compounds cannot be precipitated by nitrate of silver until the solution is boiled, when the chlorine is replaced by oxygen, the original ammonio-cobaltic salts being re-produced.

More recently, the same chemist has published a full investigation of this subject, in which he describes a numerous and interesting series of ammonio-cobaltic salts. (*Ann. de Chim. et de Phys.* 8d ser. vol. xxxv. p. 267.)

SULPHIDE OF COBALT, CoS.

This compound may be obtained by the direct combination of its elements at a high temperature, or by heating one of the oxides of cobalt with excess of sulphur. It is a gray crystalline substance, possessing a metallic lustre.

Hydrated sulphide of cobalt is thrown down as a black precipitate when an alkaline sulphide is added to a solution of cobalt-salt. The hydrate is not dissolved to any great extent by dilute hydrochloric acid, but is easily soluble in nitric acid.

When sulphate of cobalt is reduced by hydrogen, an *oxysulphide*, CoS, CoO , is formed, which is decomposed into its proximate constituents by treatment with acids.

The *sesquisulphide*, Co_2S_3 , is met with in nature in gray octohedra (*cobalt-pyrites*); it is obtained by passing sulphuretted hydrogen over sesquioxide of cobalt heated to about 500°F . (260°C .)

Bisulphide of cobalt, CoS_2 , is formed when a mixture of carbonate of cobalt and sulphur is heated to a certain point; it is a black, amorphous powder, which is decomposed by heat into sulphur and sulphide of cobalt. The bisulphide is not readily attacked by acids or alkalis.

§ 251. *Technical History of Cobalt*.—The chief minerals containing cobalt are the following:—

White cobalt ore, which is the most common, and contains cobalt associated with arsenic, iron, and sulphur.

Gray cobalt ore, containing arsenic, iron, cobalt, and silica.

Glance cobalt, or *Tunaberg cobalt*, which, when pure, has the formula $\text{CoAs}_2, \text{CoS}_2$. This is the richest of the cobalt ores. It can be dissolved only by nitric acid. These ores generally contain more or less nickel.

Since cobalt is never used in the metallic state, the reduction of the ores of this metal has for its object the production of a pretty pure oxide.

It is generally thought sufficient to roast the ore in order to expel the greater part of its arsenic and sulphur, and thus to convert it into an impure oxide, which is sent into commerce under the name of *zoffre*. Cobalt is also extracted by a process similar to that described for nickel.

Cobalt is extensively employed in the preparation of colors; two of the most important of these are *smalt* and *Thenard's blue*.

Smalt is a kind of glass colored with oxide of cobalt, and reduced to a fine powder.

In order to prepare this pigment, a quantity of zaffre is fused with sand and carbonate of potassa in a large earthen crucible; the silicic acid (sand) combines with the potassa, forming a vitreous silicate, which dissolves the oxide of cobalt, while the arsenic, iron, and nickel contained in the ore, are deposited as a metallic-looking mass of *speiss*, at the bottom of the crucible. The fused mass is reduced to a fine powder, and subsequently levigated.

Thenard's blue consists of phosphate of cobalt and phosphate of alumina, and is prepared by calcining an intimate mixture of the precipitates obtained by adding phosphate of soda to solutions of the bases in question.

VANADIUM.

Sym. V. Eq. 68.6.

§ 252. This rare metal is found in certain Swedish iron-ores, remarkable for their malleability; it is also met with in the form of vanadate of lead.

It may be obtained by heating vanadic acid with potassium in a platinum crucible, and extracting the potassa with water.

Vanadium is a white metal which dissolves in nitric acid, yielding a blue solution. It is not readily attacked by sulphuric or hydrochloric acid.

Three independent oxides of vanadium are known.

The (*prot-*) oxide, VO, is formed when vanadic acid is reduced by carbon or hydrogen at a red heat. It is an indifferent oxide.

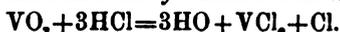
Binoxide of Vanadium, VO₂, may be precipitated as a hydrate by adding potassa to a solution of the bichloride, prepared by heating vanadic acid with hydrochloric acid. It is white when freshly precipitated, and becomes brown upon drying. When binoxide of vanadium is exposed to air, it absorbs oxygen, and assumes a greenish color, due to the formation of an intermediate oxide; it sometimes plays the part of an acid, but generally that of a base, for it dissolves in acids, forming crystallizable salts, which have a blue color.

VANADIC ACID, VO₃.

To prepare this acid, the natural vanadate of lead is heated with nitric acid, evaporated, and the residue extracted with water, which leaves vanadic acid undissolved; this latter is dissolved in ammonia, when crystals of the ammonia-salt are obtained on evaporation; this salt, ignited in air, leaves the vanadic acid.

This acid has a yellow color; it fuses at a red heat, and when cooled, solidifies again, with evolution of light; it is not decomposed at a high temperature. It is very slightly soluble in water, giving a yellow solution, which reddens litmus-paper. Organic matters, and reducing agents in general, convert vanadic acid into the oxide.

When vanadic acid is dissolved in hydrochloric acid, and the solution heated, chlorine is disengaged, and *bichloride of vanadium* formed:—



Vanadic acid combines with bases, forming crystallizable *vanadates*. The vanadates of the alkalies are soluble in water.

Vanadic acid also behaves like a basic tetroxide, in combining with acids to form definite salts, which may be crystallized; thus, the compound with sulphuric acid has the composition, VO₃.3SO₃. Similar compounds have been obtained with nitric, arsenic, and phosphoric acids. They have a yellow or red color, and are soluble; their solutions lose their color when heated, and are rendered blue by sulphuretted hydrogen and organic matters, in consequence of the reduction of the acid to the state of binoxide of vanadium.

Binoxide of vanadium also combines with vanadic acid, forming compounds which dissolve in water with a fine green color; these compounds contain, respectively, VO₃.2VO₂ and VO₃.4VO₂, and are obtained either by heating vanadic acid with the binoxide, or by adding a solution of an alkaline vanadate to a salt of binoxide of vanadium.

Terchloride of Vanadium, VCl₃, is a volatile, yellow, fuming liquid, obtained by passing chlorine over a mixture of vanadic acid and charcoal at a red heat.

Bisulphide of Vanadium, VS₂, constitutes the black precipitate which is produced by an alkaline sulphide in a salt of the binoxide; it dissolves in an excess of the precipitant, forming a purple solution.

REACTIONS OF VANADIUM.—*Potassa, soda, and their carbonates*; a grayish precipitate of hydrate, soluble in excess, yielding a blue or brown solution.

Ammonia; a brown precipitate, insoluble in excess.

Sulphide of ammonium; a dark-brown precipitate, soluble in excess, yielding a dark purple solution.

Ferrocyanide of potassium; a yellowish-green precipitate.

Hydrosulphuric acid, in acid solutions of vanadic acid, a blue color, due to reduction.

With a *borax-bead*, in the *outer flame*, a yellow glass, becoming green in the *inner flame*, and brown while hot, if much vanadium be present. If the bead contain but little vanadium, it may be perfectly decolorized in the *outer flame*.

METALS OF THE FOURTH GROUP.

CADMIUM.

Sym. Cd. Eq. 56. Sp. Gr. 8.6.

§ 253. THIS metal is associated in nature with the ores of zinc, and does not occur very frequently or in large quantities.

Preparation.—In the description already given of the extraction of zinc from its ores, it was mentioned that the first portions of the vapor which passed over when the roasted ore was distilled with charcoal, burnt with a brown flame (brown blaze), due to the presence of cadmium. In order to obtain this metal in a pure state, these vapors are condensed, and the mixture of zinc, cadmium, and a little copper, thus obtained, is dissolved in hydrochloric or sulphuric acid, and the solution treated with sulphuretted hydrogen, which precipitates the sulphides of copper and cadmium; these are washed, redissolved in concentrated hydrochloric acid; after evaporating the solution to expel excess of acid, carbonate of ammonia in excess is added, which precipitates the carbonate of cadmium, and redissolves that of copper; the carbonate is calcined to expel carbonic acid, and distilled with carbon, when metallic cadmium distils over.

Cadmium may also be obtained by collecting the oxides of zinc and cadmium resulting from the brown blaze, and distilling these, at a moderate heat with charcoal, when most of the zinc is left in the residue; by repeating the operation, the cadmium may be still further purified.

Properties.—Cadmium has a grayish-white color, and much resembles tin in its physical properties. It is very soft, malleable, and ductile; when bent, it emits a crackling sound, like tin; its internal structure is crystalline.

This metal fuses very easily, and is converted by a higher temperature into an inodorous vapor; the fused metal, if slowly cooled, crystallizes in octohedra.

Cadmium is not sensibly affected by dry air at the ordinary temperature; when heated in air, it oxidizes more readily than zinc, burning with a luminous flame, and producing a red-brown oxide. It dissolves readily in dilute acids, with disengagement of hydrogen. Hydrated alkalies also dissolve cadmium at a high temperature.

Only one oxide of cadmium, CdO, is known.

OXIDE OF CADMIUM, CdO.

The oxide is formed when cadmium is heated in air; if the metal be heated in a close crucible, the oxide condenses, as a red-brown film, upon the cover. It has a yellow, brown, or black color, according to the temperature to which it has been exposed; it is sometimes crystallized in needles.

This oxide is infusible, and does not volatilize; it combines with acids, forming well-defined salts. It is capable of absorbing carbonic acid from the air.

The *hydrated oxide* is obtained as a gelatinous precipitate, when an alkali is added to a solution of a salt of cadmium; the hydrate (CdO.HO) is white, but becomes brown when heated, from loss of water. It is easily reduced by charcoal at a low red heat.

Nitrate of Cadmium ($\text{CdO}.\text{NO}_3$) is obtained by dissolving the metal in nitric acid; it forms hydrated prisms, which are deliquescent and very soluble in water.

SULPHATE OF CADMIUM ($\text{CdO}.\text{SO}_3$) may be prepared by dissolving cadmium, its oxide or carbonate, in sulphuric acid. It crystallizes in colorless, rectangular prisms, of the formula $\text{CdO}.\text{SO}_3 + 4\text{Aq}$; they are very soluble in water, and are decomposed by a high temperature.

Anhydrous sulphate of cadmium absorbs three equivalents of ammonia.

A basic sulphate of cadmium, of the formula $\text{CdO}.\text{SO}_3, \text{CdO}.\text{HO}$, is obtained when neutral sulphate is heated, or partially decomposed by alkalis.

Basic carbonates of cadmium are obtained by the action of alkaline carbonates on solutions of cadmium-salts, varying in composition with the quantity of carbonate employed in the precipitation.

CHLORIDE OF CADMIUM, CdCl_2 .—To prepare this salt, cadmium may be heated in a current of chlorine, or may be dissolved in hydrochloric acid. It forms rectangular four-sided prisms, which are hydrated; these crystals effloresce in dry air, and lose their water when heated, subsequently undergoing the igneous fusion, and finally subliming in crystalline scales. Chloride of cadmium dissolves very readily in water, and is capable of forming double-salts with the chloride of the alkali-metals.

The anhydrous chloride absorbs three equivalents of ammonia; its solution in ammonia deposits crystals of the formula $\text{CdCl}_2.\text{NH}_3$.

SULPHIDE OF CADMIUM, CdS .—This compound is found in nature, crystallized in hexagonal prisms of a yellow color.

It may be obtained by heating a mixture of sulphur and oxide of cadmium, or by precipitating a salt of cadmium by sulphuretted hydrogen, or a soluble sulphide. Thus prepared, it has a bright-yellow color, and is employed in painting. Its color becomes red on the application of heat, and yellow again on cooling. It fuses at a red heat, and becomes crystalline on cooling. The precipitated sulphides dissolve readily in acids.

Neither cadmium nor its compounds have received any very important application in the arts.

COPPER.

Sym. Cu. Eq. 81.7. Sp. Gr. 8.8.

§ 254. In describing this metal, we shall pursue the same course as with iron.

Copper is found abundantly in nature, both in the pure state, and in combination; the ores of copper will be described hereafter.

Commercial specimens of copper are often sufficiently pure for most chemical purposes. Copper-turnings are frequently employed in the laboratory; in order to free them from the grease with which they are usually contaminated, they are heated to redness in air, until covered with a superficial coating of black oxide; they are then introduced into a piece of combustion-tube, through which a stream of pure and dry hydrogen is passed; when the apparatus is filled with hydrogen, the tube is heated, either by a charcoal-furnace or a gas-flame, and the hydrogen passed over the heated turnings, until no more steam is evolved, and the copper appears to be free from oxide; the metal should be allowed to cool in an atmosphere of hydrogen.

Pure copper may also be obtained, in a finely-divided state, by reducing the oxide, at a high temperature, by means of hydrogen.

A very good method of obtaining small, compact masses of copper, consists in reducing the metal from the pure sulphate by the electrolytic process.

Properties.—Copper has a red-brown color, and is capable of a high lustre;¹ it is a very malleable and ductile metal. Only two metals, gold and silver, are more malleable than copper; in ductility it ranks after gold, silver, platinum, and iron; only the latter metal surpasses it in tenacity; a copper wire of one-tenth of an inch in diameter, is capable of supporting a weight of 885 pounds. It is the most sonorous of metals. Copper is not so hard as iron; it has a metallic taste, and a disagreeable smell when rubbed. The specific gravity of copper varies from 8.78 to 8.96, according as it has been cast or drawn into wire.

This metal fuses at a bright-red heat, and at a white heat is slightly volatile; its vapor burns with a fine green flame, which is perceived when a copper-wire is heated in the flame of a gauze-burner. When fused copper is allowed to cool gradually, it crystallizes in rhombohedra. It is precipitated from its solutions, by other metals, in small cubical crystals. This metal is unaltered by exposure to dry air or oxygen; in moist air it becomes covered with a coating of oxide, which absorbs carbonic acid, and is converted into a green basic carbonate.

When copper is heated in air, it becomes covered, at first, with a red film of suboxide, which passes ultimately into the black oxide. It does not decompose water at the ordinary temperature, even in presence of acids; at a white heat, it is capable of decomposing it to a slight extent only.

Nitric acid easily dissolves copper, with evolution of binoxide of nitrogen:—



When copper is exposed to air, in contact with solution of ammonia, it is converted into oxide of copper, which dissolves in ammonia, forming a blue solution.

Hydrochloric acid dissolves copper to a slight extent, probably, however, only with the co-operation of atmospheric oxygen.

A dilute solution of chloride of sodium is capable of dissolving copper, though a concentrated solution scarcely affects it.²

Strong sulphuric acid dissolves copper with the aid of heat, sulphurous acid being evolved:—



According to some authorities, the sulphate of suboxide of copper is also formed in this case.

Copper is easily oxidized when exposed to air in presence of acids or of fatty matters; hence this metal can only be used for a few culinary purposes with perfect safety, since its compounds are very poisonous.

Copper combines directly with most of the elements, and, in some cases, very energetically.

COPPER AND OXYGEN.

Suboxide	Cu_2O
(Prot-) oxide	CuO
Bin oxide	CuO_2

and a higher oxide, the composition of which is not known; it has been termed cupric acid.

SUBOXIDE, OR RED OXIDE, OF COPPER, Cu_2O .

§ 255. The red oxide of copper is found in nature as *red copper-ore*.

¹ Copper in a state of extreme tenuity has a green color by transmitted light.

² The effect of a solution of salt upon metallic copper is probably to be ascribed to the formation of galvanic circles between the copper and the small particles of foreign metals and other impurities existing in it.

Preparation.—I. Suboxide of copper is obtained when a mixture of the subchloride with carbonate of soda is calcined; the residue is washed with water, to remove the chloride of sodium and the excess of carbonate of soda.

II. A mixture of 5 parts of (prot-) oxide of copper and 4 parts of copper-filings may be strongly heated in a closed crucible.

III. A solution of sulphate of copper is mixed with a quantity of sugar-solution (which has been previously boiled with a few drops of dilute sulphuric acid, to convert the cane-sugar into grape-sugar), and potassa added until the precipitate at first produced is redissolved to a violet-blue fluid; on boiling this for some time, the suboxide of copper is precipitated.

Properties.—By the first and third processes, the suboxide is obtained in a crystalline state; it has a fine red color, and is not altered by exposure to air. When heated, it fuses easily, and if air be allowed access, is converted into the (prot-) oxide.

Nitric acid oxidizes the suboxide of copper, and dissolves it in the form of nitrate of (prot-) oxide.

Suboxide of copper is a feeble base.

Treated with concentrated hydrochloric acid, it yields water and subchloride of copper, which dissolves in the acid:—



Dilute acids generally decompose it into metallic copper, and the (prot-) oxide which dissolves in the acid.

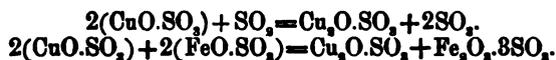
The suboxide dissolves in ammonia, forming a colorless liquid, which, when exposed to air, rapidly absorbs oxygen, and becomes blue; if the blue solution be kept in a closely stoppered bottle, in contact with copper, it again becomes colorless.

Suboxide of copper imparts a fine red color to fluxes, and is hence used for coloring glass; with access of air, the color passes into green, from the conversion of the suboxide into oxide.

Hydrated Suboxide of Copper, $4\text{Cu}_2\text{O} \cdot \text{HO}$, is prepared by decomposing the subchloride of copper with potassa. It dissolves in acids, forming the salts of suboxide of copper. The hydrate has a yellow color, and is rapidly oxidized in air, it should therefore be dried *in vacuo*.

The salts of suboxide of copper possess little practical interest.

A solution of *sulphate of suboxide of copper* may be prepared by reducing a solution of the sulphate of the (prot-) oxide with sulphurous acid or sulphate of iron:—



OXIDE OR PROTOXIDE OF COPPER, BLACK OXIDE.

CuO . Eq. 39.7.

This oxide is also occasionally found in nature. It is formed when copper is heated in air.

Preparation.—Metallic copper is oxidized by nitric acid, the mass dried, and heated in a Hessian crucible until no more fumes of peroxide of nitrogen are evolved; the mass should be stirred occasionally.

It is also prepared by mixing the nitrate of copper with half its weight of copper-filings, exposing the mixture to the air, and igniting the basic nitrate thus obtained.

Properties.—Oxide of copper is a black powder, which is very hygroscopic. When strongly heated, it fuses, and at a very high temperature loses part of its oxygen, being converted into a compound of suboxide and oxide of copper.

Oxide of copper is quite insoluble in water, but dissolves in acids, yielding important salts.

This oxide is easily reduced, at a moderately high temperature, by carbon or hydrogen, or by organic substances containing these elements, and this property renders it useful in the ultimate analysis of organic substances.

When oxide of copper is fused with hydrate of potassa or soda, it combines with the alkali to form a blue or green mass, which is decomposed by water; by allowing the fused mass to cool slowly, tetrahedral crystals of oxide of copper have been obtained.

Hydrated Oxide of Copper $\text{CuO} \cdot 2\text{H}_2\text{O}$ (*dried in vacuo*), is obtained as a blue precipitate by decomposing a solution of a copper-salt with an excess of potassa; if too little alkali be added, a basic copper-salt is precipitated. The hydrate is very unstable; if it be boiled with the liquid in which it is suspended, it is at once converted into the dense, black, anhydrous oxide; the same change takes place, though more slowly, when the precipitated hydrate is exposed to the air. The pigment known as *blue verditer* consists of hydrated oxide of copper. The hydrate dissolves very readily in acids; it is also soluble in ammonia, forming a fine blue liquid. Two definite compounds of oxide of copper, ammonia, and water, have been obtained; viz. $\text{CuO} \cdot 2\text{NH}_3 \cdot 4\text{H}_2\text{O}$, and $8\text{CuO} \cdot 2\text{NH}_3 \cdot 6\text{H}_2\text{O}$.

The hydrate dissolves to a slight extent in cold concentrated solutions of potassa and soda, forming blue liquids, which deposit the anhydrous oxide when heated. Oxide of copper is occasionally employed to impart a blue or green color to glass. The salts of oxide of copper have generally a blue or green color, and are very poisonous; their solutions have an acid reaction.

NITRATE OF OXIDE OF COPPER, NITRATE OF COPPER.



§ 256. This salt is prepared by dissolving copper in moderately strong nitric acid, and evaporating to crystallization.

It forms dark blue prismatic crystals, which contain 4 or 6 equivalents of water, according to the temperature at which they have been deposited; those with 4 eqs. are the more common. These crystals deliquesce in air, and are very soluble in water; they dissolve also in alcohol. The crystals with 6 eqs. of water are lighter in color. Anhydrous nitrate of copper is not known; when the crystals are heated, they are converted, first, into a sparingly soluble basic nitrate, of the formula $4(\text{CuO} \cdot \text{NO}_3)$, and subsequently into oxide.

Nitrate of copper is capable of oxidizing some metals with considerable energy; thus, if a crystal of this salt be wrapped in a piece of tin-foil, and struck with a hammer, the tin is converted into benzoide with a sort of explosion; again, ignition is observed when a little of the nitrate is placed on tin-foil, a very small quantity of water added, and the foil tightly wrapped up.

When a solution of nitrate of copper is treated with a small quantity of ammonia, the above-mentioned basic salt is obtained as a blue precipitate, which readily dissolves in excess of ammonia. The solution deposits a blue crystalline substance when ammonia is added in excess.

By passing ammonia gas over a concentrated solution of nitrate of copper, and over a concave glass, crystals have been obtained, of the formula $\text{CuNH}_3 \cdot \text{NH}_3 \cdot \text{NO}_3$, which is a compound of ammonia of copper with nitrate of ammonia.

SYNOPSIS OF THE SALTS OF COPPER. SULPHATE OF COPPER. BLUE

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Cu_2SO_4 $\text{Cu}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ $\text{Cu}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$

Cu_2SO_4

Preparation. This salt is commonly obtained by roasting copper-pyrites CuFeS_2 , and the excess of iron which the sulphides are, in part, converted

into sulphates, which may be extracted with water and purified by crystallization; the blue vitriol thus obtained always contains much sulphate of iron.

If too low a temperature be applied in roasting the copper-pyrites, sulphate of iron only is formed, which would, however, be decomposed if the proper degree of heat had been applied, and would become, in great measure, insoluble.

Another process consists in heating old pieces of copper in contact with sulphur, air being excluded, and thus converting them superficially into subsulphide of copper, Cu_2S , which is then roasted in air, and converted into a basic sulphate, and the latter, heated, with diluted sulphuric acid, is converted into sulphate.

It is also prepared by moistening copper-turnings with dilute sulphuric acid, exposing them to the air for some hours, and repeating the treatment with the acid until the copper is entirely converted into sulphate.

Considerable quantities of sulphate of copper are obtained as a by-product in that step of the process of silver-refining which consists in reducing that metal from the sulphate by means of copper.

In order to obtain perfectly pure sulphate, pure oxide of copper should be dissolved in sulphuric acid.

Properties.—Sulphate of copper forms fine, transparent, blue, oblique rhombic prisms, of the formula $\text{CuO.SO}_3.\text{HO}+4\text{Aq}$; these are occasionally opaque in parts, from the presence of some sulphate of copper destitute of water of crystallization; this is especially the case when the crystals are deposited from a strongly acid solution.

Exposed to dry air the crystals lose 2 eqs. water, and become opaque; at 212°F . (100°C .) they lose all their water of crystallization, and crumble to a bluish-white powder, of the formula $\text{CuO.SO}_3.\text{HO}$; the water of constitution is expelled at about 390°F . (199°C .), leaving the anhydrous salt as a grayish powder, which becomes blue immediately when in contact with water, with which it combines very energetically. At a very high temperature the salt is completely decomposed.

Crystallized sulphate of copper dissolves in 4 parts of cold, and 2 of boiling water, yielding a blue solution, which has an acid reaction, and a nauseous metallic taste. This salt is insoluble in alcohol. It is very poisonous.

The water of constitution in sulphate of copper may be replaced by an alkaline sulphate, a crystallizable double-salt being thus produced.

Sulphate of copper is capable of combining in variable proportions, with the sulphates of iron, zinc, and nickel, with which it is isomorphous. The salts thus formed contain 5 equivalents of water when the sulphate of copper predominates, and 7 equivalents when this forms the smaller portion of the compound.

Anhydrous sulphate of copper absorbs dry ammonia, forming a compound represented by $2(\text{CuO.SO}_3),5\text{NH}_3$. It also forms a hydrated compound with ammonia, which will be presently described.

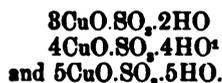
According to Kane, crystallized sulphate of copper, when dissolved in hydrochloric acid, causes considerable depression of temperature, and yields a green liquid, from which chloride of copper alone is deposited upon evaporation, provided not less than 1 equivalent of the acid has been used for each equivalent of salt; on allowing the crystals to remain for some time in contact with the mother-liquor, which contains all the sulphuric acid, crystals of blue vitriol are reproduced. Powdered crystals of sulphate of copper eagerly absorb hydrochloric acid, evolving much heat, and losing water; a green mass is obtained, which is very deliquescent, and fumes in air.

Uses.—This salt is sometimes used in medicine as an emetic and escharotic. It is also employed to prevent smut in grain. Sulphate of copper is, moreover, used in dyeing, and in the electrotype process. The anhydrous salt has been applied to the abstraction of water from alcohol.

The blue vitriol of commerce is often contaminated with the sulphates of iron and zinc; in order to ascertain the purity of a specimen, its solution should be

acidified with hydrochloric acid, the whole of the copper precipitated by a rapid current of sulphuretted hydrogen, and the filtered liquid (shown to be free from copper by adding more sulphuretted hydrogen) concentrated by evaporation with a few drops of nitric acid, tested for iron by adding an excess of ammonia, and subsequently for zinc, with sulphide of ammonium, after filtering off the iron precipitate.

Three basic sulphates of copper have been examined, and are composed respectively of



They are obtained either by digesting solution of the neutral sulphate with the hydrated oxide, or by decomposing that salt with an insufficient quantity of potassa.

Ammonio-sulphate of Copper, $\text{CuO} \cdot \text{SO}_4 \cdot 2\text{NH}_3 \cdot \text{HO}$.—When sulphate of copper is dissolved in solution of ammonia, fine crystals of the above formula may be obtained by spontaneous evaporation; these crystals are celebrated for their remarkably fine blue colour; the *ammoniated copper* of the pharmacopœia, prepared by triturating 2 parts of crystallized sulphate of copper with 3 parts of sesquicarbonate of ammonia, is probably a compound of sulphate of copper with sulphate of ammonia, containing also the above combination of sulphate of copper with ammonia, and probably a basic sulphate of copper; its formation is attended with evolution of much carbonic acid, showing that part of the ammonia is converted into sulphate.

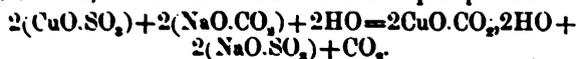
CARBONATES OF COPPER.

The *Neutral Carbonate of Copper* ($\text{CuO} \cdot \text{CO}_2$) is found in nature as the rather rare mineral *mysorine*; it occurs in earthy masses, of a dark-brown color.

BIBASIC CARBONATE OF COPPER, $2\text{CuO} \cdot \text{CO}_2 \cdot \text{HO}$.—This compound forms the mineral *malachite*, which sometimes serves as an ore of copper.

Malachite is a very hard mineral, of the spec. grav. 3.5; it is sometimes found crystallized, but generally in compact concentric masses, of a fine green color; it dissolves easily in acids. This mineral is occasionally used for ornamental purposes.

When a solution of a copper-salt is decomposed by an alkaline carbonate, carbonic acid is evolved, and the above basic carbonate precipitated:—



This precipitate has a blue color, and is very bulky, but if it be gently heated with the supernatant liquid, it becomes granular and green, having now the formula $2\text{CuO} \cdot \text{CO}_2 \cdot \text{HO}$. This latter compound is used as a pigment, under the name of *mineral green*.

When long boiled with the supernatant liquid, the precipitate is converted into black oxide of copper.

Sesquibasic Carbonate of Copper, $3\text{CuO} \cdot 2\text{CO}_2 \cdot \text{HO}$.—This carbonate is found in nature as *blue malachite*, *mountain-blue*, or *copper-azure*, and is employed as a color.

A *Tribasic Carbonate*, of the formula $3\text{CuO} \cdot \text{CO}_2$, is said to exist.

An *ammoniacal carbonate of copper*, $\text{CuO} \cdot \text{CO}_2 \cdot \text{NH}_3$, has been obtained by dissolving the bibasic carbonate in carbonate of ammonia, and adding alcohol; it crystallizes in fine blue needles.

Compounds of carbonate of copper with carbonate of potassa or of soda may be crystallized from a solution of the bibasic carbonate of copper in the bicarbonate of one of these bases.

[†] This salt is found in nature as the mineral *Brockentite*.

The *silicate of copper* forms the rare mineral *diopside*, or *emerald copper-ore*, so termed from the transparent green color of its hexahedral crystals. *Chrysocolla* is also a silicate of copper.

BINOXIDE OR PEROXIDE OF COPPER, CuO_2 .

§ 257. This oxide has been obtained by the action of binoxide of hydrogen on hydrated oxide of copper. It has a yellowish-brown color, and is very easily decomposed into oxygen and oxide of copper by heat or acids.

CUPRIC ACID.

This acid is not known in the separate state; it is formed as a potassa-salt when finely-divided copper is fused with hydrate of potassa and nitre, or when hydrated oxide of copper is dissolved in a solution of hypochlorite of potassa.

The potassa-salt is exceedingly unstable; its aqueous solution is blue, and is very easily decomposed into potassa, oxygen, and oxide of copper, which is precipitated.

A *compound of copper with hydrogen*, of the formula Cu_2H , has been obtained by Wurtz, by the action of hypophosphorous acid upon solution of sulphate of copper.

It is a brown powder, easily decomposed into its elements by heat, oxidizing in air, and dissolving in hydrochloric acid, with disengagement of hydrogen.

Schrötter has obtained a *compound of copper with nitrogen*, to which he has assigned the formula Cu_2N , by passing ammonia over oxide of copper, heated to 509°F . (265°C .), and removing the excess of oxide from the resulting compound by treatment with solution of ammonia.

This compound forms a dark-green amorphous powder, which is decomposed with some violence below a red heat, and dissolves in hydrochloric acid, forming chloride of copper and sal-ammoniac.

SUBCHLORIDE OF COPPER, Cu_2Cl .

§ 258. *Preparation*.—I. A solution of chloride of copper is mixed with hydrochloric acid, and boiled with metallic copper, until the green colour of the solution has changed to brown; the clear liquid is then rapidly decanted, and mixed with a large quantity of water, which precipitates the subchloride; the precipitate must be washed by decantation, as rapidly as possible, with water which has been freed from air by boiling, and preserved under a layer of water in a well-stoppered bottle.

II. Solution of chloride of copper is mixed with a concentrated solution of (proto-) chloride of tin, containing a little free acid, when the subchloride is precipitated:—



III. Copper is heated to redness in a current of chlorine.

IV. Chloride of mercury is distilled with copper filings.

Properties.—Subchloride of copper is white; it fuses below a red heat, and volatilizes at a higher temperature. When exposed to the air, it is converted into a green compound of oxide and subchloride. It is nearly insoluble in water, but dissolves in hydrochloric acid, and forms a brown liquid, from which water precipitates the subchloride. The salt may be crystallized from the hydrochloric solution, in tetrahedral crystals.

Ammonia readily dissolves the subchloride, giving a colorless solution which rapidly becomes blue, from oxidation, when exposed to air. This solution is sometimes employed to absorb oxygen from gaseous mixtures.

Subchloride of copper is decomposed by the fixed alkalis, the hydrated suboxide being formed.

CHLORIDE OR PROTOCHLORIDE OF COPPER, CuCl .

Anhydrous chloride of copper may be obtained by heating the metal in an excess of chlorine, when, if finely divided, it undergoes combustion.

The anhydrous chloride has a yellowish-brown color. When heated to dull redness, it loses chlorine, and Cu_2Cl is left.

Hydrated chloride of copper is prepared by dissolving the oxide in hydrochloric acid, and evaporating. It forms beautiful green needles, of the formula $\text{CuCl} + 2\text{Aq}$; they are deliquescent, and very soluble in water; the solution is blue when diluted, and has a green color when concentrated, or when mixed with a large quantity of hydrochloric acid.

Chloride of copper is easily soluble in alcohol, to the flame of which it imparts a green colour.

The anhydrous chloride is capable of absorbing 3 eqs. of ammonia, forming a blue compound.

When ammonia is passed into a hot solution of chloride of copper, a compound is formed which crystallizes, on cooling, in dark blue prisms, of the formula $\text{CuCl} \cdot 2\text{NH}_3 \cdot \text{HO}$. At 300°F . (149°C .) these are decomposed, leaving $\text{CuCl} \cdot \text{NH}_3$.

OXYCHLORIDES OF COPPER.—Three compounds of chloride and oxide of copper are known, containing one equivalent of the former compound, and two, three, or four equivalents of the latter.

The oxychloride having the formula $\text{CuCl} \cdot 3\text{CuO} \cdot 4\text{HO}$, is precipitated when a solution of chloride of copper is decomposed with an insufficient quantity of potassa.

This compound is used in painting, under the name of *Brunswick green*, and is prepared on a large scale by moistening copper with hydrochloric acid, or solution of sal-ammoniac, and exposing it to the air, when it becomes covered with a green coating of the above oxychloride.

This oxychloride is found crystallized in the mineral kingdom, as *atacamite*.

COPPER AND SULPHUR.

Subsulphide of copper.	Cu_2S .
Sulphide "	CuS .

SUBSULPHIDE OF COPPER. Cu_2S .

§ 259. The subsulphide exists in nature, and forms one of the richest ores of copper (*copper-glance*). Its crystalline form is the six-sided prism; it is soft, and has a feeble metallic lustre. This ore usually contains a little iron and silver.

It may be artificially obtained by heating 3 parts of sulphur with 8 parts of copper-turnings, when combination takes place with disengagement of heat and light.

This sulphide fuses more easily than the metal, and is not decomposed by heat; when roasted in air, it is partly converted into sulphate; it is not attacked by hydrochloric acid, but is dissolved by nitric and nitro-hydrochloric acids.

Subsulphide of copper is not decomposed by hydrogen, and is reduced with difficulty by carbon.

When fused with caustic alkalis, metallic copper is separated.

If a mixture of subsulphide of copper and sulphate of copper be strongly heated, the copper is reduced:—



This sub sulphide is sometimes found crystallized, in octohedra, in the copper-smelting furnaces.

SULPHIDE OF COPPER, Cu_2S .

This sulphide occurs in nature as *indigo-copper*, or *blue-copper*; it is precipitated by decomposing a solution of a copper-salt with hydrosulphuric acid or a soluble sulphide.

It is a black powder, which, when exposed to the air, especially in a moist state, soon becomes green, from production of sulphate of copper.

When heated in close vessels, or in an atmosphere of hydrogen, it is converted into Cu_2S .

Sulphide of copper is not attacked by boiling in moderately dilute sulphuric acid; hydrochloric acid scarcely affects it, but nitric acid dissolves it readily, sulphur being separated.

This sulphide is insoluble in sulphide of potassium, but dissolves in small quantity, in yellow sulphide of ammonium.

Higher sulphides of copper are said to be precipitated from solutions of copper-salts by the polysulphides of the alkali-metals.

An *Oxysulphide of Copper*, of the formula $5\text{CuS}\cdot\text{CuO}\cdot\text{HO}$ is precipitated, according to Pelouze, when a soluble sulphide is added to a boiling solution of nitrate of copper mixed with excess of ammonia.

COPPER-PYRITES, $\text{Fe}_7\text{S}_8\cdot\text{Cu}_2\text{S}$.

This is one of the commonest ores of copper.

It has a fine brass-yellow color, and a metallic lustre, and is found crystallized in forms derived from the octohedron.

The spec. grav. of copper-pyrites is 4.17; it fuses at a moderate heat; when heated in air, it yields the sulphates, and ultimately the oxides of iron and copper, sulphurous acid being disengaged.

It is not acted on by hydrochloric acid, but nitric and nitro-hydrochloric acids readily dissolve it.

Variogated Copper-ore (peacock ore) is also composed of sulphur, iron, and copper, but in variable proportions. It is distinguished by its beautifully iridescent appearance, due probably to a superficial oxidation. Variogated copper-ore is generally amorphous, but sometimes crystallized in forms derived from the cube; its specific gravity is 4.98, and it is fused, but not decomposed, when heated in close vessels. It is dissolved by nitric acid.

PHOSPHIDES OF COPPER.—Copper may be made to unite, at a red heat, with about twenty per cent. of phosphorus, to form a gray, hard, brittle mass, of metallic appearance, and more fusible than copper.

When hydrogen is passed over phosphate of copper at a moderately high temperature, a phosphide of the formula Cu_3P is obtained. Another phosphide of copper (Cu_2P) is thrown down as a black precipitate when phosphuretted hydrogen is passed into a solution of a copper-salt. Other phosphides appear to exist.

METALLURGY OF COPPER.

§ 260. The chief ores of copper are the following:—

Native copper (the metal itself), which is found crystallized in cubes and six-sided prisms.

Red copper-ore, composed of the suboxide, generally associated with sesquioxide of iron.

Black oxide of copper.

Blue carbonate of copper, $3\text{CuO}\cdot 2\text{CO}_2\cdot\text{HO} = 2(\text{CuO}\cdot\text{CO}_2) + \text{CuO}\cdot\text{HO}$.

Malachite, $\text{CuO}\cdot\text{CO}_2 + \text{CuO}\cdot\text{HO}$.

Subsulphide of copper, Cu_2S (*copper-glance*).

Copper-pyrites, $\text{Fe}_2\text{S}_3, \text{Cu}_2\text{S} = 2(\text{FeCuS}_2)$

Variogated copper-ore.

Gray copper-ore, containing sulphides of copper, antimony, arsenic, lead, and silver.

All these ores are more or less used for the extraction of copper, but this is the case chiefly with copper-pyrites and gray copper-ore, and since these are the most difficult to reduce, a description of the process employed to effect that purpose will best exhibit the general principles of the smelting of copper-ores.

The ore freed from gangue, is first roasted on the hearth of a reverberatory furnace by the flame of a coal-fire; during this process, part of the sulphur is volatilized, another portion is converted into sulphurous acid, and the remainder into sulphuric acid, which is left in combination with the oxides of iron and copper; moreover, part of the arsenic is expelled as arsenious acid or as a sulphide of arsenic, and the rest is left in the form of an arseniate. The roasted ore, therefore, consists chiefly of oxides of copper and of iron, of unaltered sulphides of these metals, and of arsenic acid. It is now fused in another reverberatory furnace, with some oxidized silicious slags from a former operation, and some oxidized ores of copper; a quantity of fluor-spar being also added, to promote the fusion of the slag. In this operation, the oxides and sulphides undergo a mutual decomposition, the copper combining chiefly with the sulphur, whilst the iron takes the oxygen, and passes into the slag, which consists chiefly of silicate of oxide of iron. A product is thus obtained which contains about 33 per cent. of copper, combined chiefly with sulphur; it is run out into a cistern of water, and thus granulated.

This is again oxidized by roasting, and afterwards fused with certain ores and slags rich in oxide of copper, which, by a double decomposition, converts almost all the sulphide of iron into a sulphide of copper and oxide of iron, the latter combining with the silica to form a fusible slag. The result of this operation is a subsulphide of copper containing very little iron, arsenic, and other impurities of the original ore; it is roasted in a peculiar manner, with access of air, which oxidizes the greater part of the impurities, and the crude copper is afterwards refined by fusion in contact with air, and with a little silica, by which the whole of the sulphur is removed, and the foreign metals are oxidized and dissolved in the slag. But the copper thus obtained contains still a little suboxide, which affects its malleability; it is purified by fusion in contact with charcoal, and stirring with a pole of green wood, which disengages highly reducing gases.

The copper is then in a marketable state.

Copper ores are sometimes worked for silver and copper at the same time, when, of course, other processes are had recourse to for the economical separation of these metals.

According to Brankart's process, a certain amount of copper is obtained by reducing, with metallic iron, the solution of sulphate of copper obtained by washing the roasted sulphureous ores with water.

The process of *Rivot and Phillips* consists in reducing the ores, previously oxidized by roasting, by means of metallic iron at a high temperature.

Napier's process depends upon the same principle, the abstraction of the sulphur being assisted by the employment of *soda-ash* or *salt-cake*. The sulphide of sodium then formed is afterwards removed by treating the crude metal with water, which also dissolves the sulphur-salts of antimony and tin, thus entirely removing these metals, which would much injure the quality of the copper.

The best specimens of commercial copper are nearly pure; they contain only traces of iron. A very small quantity of arsenic or of phosphorus injures the color of the metal, rendering it whitish, at the same time causing it to be somewhat brittle.

USES OF COPPER.

§ 261. This metal is chiefly employed for sheathing the bottoms of ships, to protect them from the action of sea-water, and to diminish the friction of the latter upon the bottom and sides of the vessel. It is, moreover, largely used for boilers, stills, and culinary vessels.

Copper-plates are used for engraving; they are covered with a particular varnish, through which the subject is engraved with a tool; the plate is then acted on by nitric acid, which eats into the lines of the engraving, leaving the varnished portion untouched; the varnish is then cleaned off, and the work finished by graving-tools. But the largest quantity of copper is employed for making various highly important alloys. We must not omit to mention the use of copper for coinage.

Alloys of Copper and Zinc.—Copper may be readily alloyed with zinc, which materially alters its physical properties; a small quantity of this last metal changes the red color of copper to a shade of yellow, which passes through various gradations as the quantity of zinc is increased, until it arrives at a bluish-gray.

The specific gravity of an alloy of copper and zinc is generally higher than would be expected from the mere mixture of the two metals, rendering it probable that a combination has taken place.

The alloys of copper and zinc are more fusible than copper itself, and lose part of their zinc at high temperatures; this metal may be expelled almost entirely by a strong heat. When they are fused in contact with air, a film of oxide of zinc is formed upon the surface, and if this be removed, from time to time, the whole of the zinc may be extracted from the alloy.

A little lead added to these alloys prevents them from "greasing the file," *i. e.* filling up the cavities of that tool. Tin hardens the alloys.

The most important alloys of copper and zinc are *brass*, *Dutch gold*, *pinchbeck*, and *tombac*.

Brass differs in composition according to the purposes to which it is to be applied, but it always consists of about $\frac{3}{4}$ copper and $\frac{1}{4}$ zinc, with small quantities of lead (varying from 2 to 0.5 per cent.) and of tin (from 0.25 to 0.5 per cent.).

At the present day, brass is generally prepared by the direct combination of the metals, but formerly it was customary to fuse metallic copper with calamine and charcoal.

Tombac, which is employed for articles intended for gilding, generally contains from 10 to 14 per cent. of zinc.

Alloys of Copper and Tin.—Although we have not yet described the properties of tin, yet since copper forms several alloys with it which contain this metal (copper) as their principal ingredient, we will remark upon them in this place.

Tin does not easily combine with copper, and the compound, when formed, is very easily decomposed; a portion of the tin is separated in the liquid form when the alloy is gradually heated, or allowed to cool slowly from the fused state.

An alloy of tin and copper is much harder than either of these metals, and was used by the ancients for making swords and knives, before iron was employed for these purposes. When such alloys are allowed to cool slowly, they become hard, and sometimes brittle, but they may be rendered malleable by being heated to redness and plunged into water; just the opposite effect to that which this treatment has upon steel.

The two metals may be entirely separated by fusing the alloy for a sufficient length of time in contact with air, when the tin is oxidized.

The specific gravity of alloys of copper and tin is higher than that of a mixture of these metals should be.

The chief alloys of copper and tin are *bronze*, *gun-metal*, *bell-metal*, *speculum-metal*, and the metal of which certain musical instruments (cymbals, &c.) are made.

Bronze varies much in the proportions of copper and tin which it contains; small quantities of iron, zinc, and lead are often added to it.

GUN-METAL (employed for pieces of ordnance) should possess great tenacity, considerable hardness, and a moderate fusibility, in order that it may be easily cast into moulds. The only metals, possessing considerable tenacity, which can be used for this purpose, are copper and iron; the latter, when pure, is, however, too infusible; and the comparatively small tenacity of cast-iron renders it necessary to give to guns of this material a thickness which would render them useless in service requiring rapid transport of artillery; this metal is therefore almost exclusively employed for guns of heavy caliber. Copper is too soft to be employed in the pure state, its hardness is therefore increased by adding a quantity of tin insufficient to diminish to any great extent the tenacity of the copper.

In consequence of the tendency exhibited by the alloys of copper and tin to separate into their constituents, the guns never have a uniform composition throughout, however perfectly the mixture of metals was effected during the fusion, the proportion of tin being found to increase gradually from the breech to the muzzle of the gun.

The alloy of which the smaller cannon are made, consists, with slight variations on either side, of

Copper	90.5
Tin	9.5
		100.0

The proportion of tin is sometimes slightly increased in guns of larger caliber. Since a certain quantity of tin is always separated by oxidation during the fusion, it is necessary to employ originally a quantity of that metal in addition to the above proportion. The alloy is prepared by fusing together copper, tin, old gun-metal, and bronze. The copper employed is almost chemically pure; the tin is also very pure; Banca tin (Cornwall) is preferred.

The reverberatory furnace in which the fusion is effected is so constructed that no air shall enter which has not been deoxidized by passing through a layer of ignited fuel, and the draught-holes are so arranged that the flame is forced to spread itself over the hearth.

The alloy was formerly prepared by first fusing together the old gun-metal, the bronze, and the copper, and afterwards adding the tin; but the latter metal was always found to be very unequally distributed, portions occurring in the alloy which contained a very large percentage of tin; it has therefore been found far better first to alloy the tin with copper, in the proportions contained in speculum-metal (2Cu to 1Sn), and afterwards to add this alloy to the fused mixture of gun-metal and copper. In this way a far more complete admixture of metals is effected, and the loss of tin by oxidation is less, since the metal need not be maintained in fusion for so long a period as in the former case. Long wooden stirrers are used to mix the metals thoroughly, and at the same time to deoxidise them. When the fusion is completed, and mixture is perfect, the oxide is removed from the surface, and the metal run into moulds formed of loam and sand (which give to it merely its external form), the gun being cast perpendicularly, the muzzle upwards. In the original casting, the latter is lengthened into a cylindrical mass of metal, about 3 feet high, which is afterwards cut off, before the gun is turned and bored. The object of adding this superfluous portion to the casting, above the gun, is, by the pressure of this column of fused metal, to render the solidification more rapid, thus allowing the metals less time to separate, and to increase the density of the alloy at the breech of the gun, where the greatest tenacity is required. Particles of oxide, or dross, will also rise into

this portion of the casting when the metal is fluid; any defects which they might occasion in the gun are thus obviated.

Bell-metal contains usually about 1 part of tin, and 3 of copper; small quantities of zinc and lead are sometimes added; these diminish the sonorosity of the compound.

Speculum-metal, employed in making telescopes, consists of 1 part of tin, and 2 of copper, and generally contains a little zinc, arsenic, and silver; it is a hard, brittle alloy, capable of a high polish.

The metal of which musical instruments are made, contains 4 parts of copper, and 1 of tin.

The alloy known as *pack-fong*, *argentan*, or, more commonly, *German silver*, consists of 2 parts of copper, 1 of nickel, and 1 of zinc. The copper and nickel are first fused together, and the zinc afterwards added.

German silver has a yellowish-white color, is malleable and ductile. It should not be employed in making culinary vessels, since it is easily oxidized and dissolved by contact with air and acids.

For some purposes, copper is covered with a thin layer of tin, by spreading the fused metal over the heated surface of copper to which it adheres.

Pins made of brass wire are tinned by boiling with bitartrate of potassa, granulated tin, and water; the tin is oxidized at the expense of the latter, and dissolved by the bitartrate of potassa; from this solution, it is deposited in the metallic state upon the pins, which reduce it by galvanic action.

§ 262. ASSAY OF COPPER-ORES.—The ores of copper are assayed by different methods, according to the nature of their constituents.

They may be conveniently divided into three classes.

1st class. Ores containing no other metals besides copper and iron, and which are perfectly free from sulphur and arsenic.

2d class. Ores similar to the above, but containing sulphur.

3d class. Ores containing other metals besides copper and iron.

Assay of Ores belonging to the 1st Class.—About 400 grs. of ore are mixed with 3 times their weight of black flux, and gradually heated in an earthen crucible placed in a coke fire, the heat being at last raised to bright redness, and this temperature maintained for about fifteen minutes. The copper is thus reduced to the metallic state, and fused into a button at the bottom of the crucible. When cool, the latter is broken, the button carefully extracted, and weighed.

If the ore be very poor, it is usual to fuse it with a quantity of sulphur, in the same manner as if it were an ore of the 2d class.

Assay of Ores belonging to the 2d Class.—The powdered ore is mixed with an equal weight of dried borax, and fused in an earthen crucible, at a dull red heat. In this way the earthy matters (*gangue*) are separated from the sulphide of copper, which forms a button (*matte*) at the bottom of the crucible. The contents of the latter are then poured into an elliptical iron mould (*scorifier*), and the slag separated from the button by means of a hammer.

The button, or *matte*, is then finely powdered in an iron mortar, and introduced into an earthen crucible, which is placed obliquely in a furnace, the draught of which is almost entirely cut off, so that only a gentle heat is obtained. In this way, the ore is roasted for some time, and constantly stirred with a steel rod. The heat is gradually raised, and when no more sulphurous acid is evolved, the crucible is exposed for a few minutes to a white heat (in order to decompose the sulphates), and removed from the fire.

The roasted ore is now mixed with 3 or 4 parts of black flux, returned to the same crucible, covered with a layer of fused borax, and heated for twenty minutes in a wind-furnace. The crucible is then allowed to cool, the button extracted by

breaking the crucible, and weighed, after removing all adhering impurities by gently striking it with a hammer. .

Assay of Ores of the 3d Class.—The powdered ore is first fused as in the preceding case, to obtain a matt, which is then roasted, very gradually, so as not to fuse the ore, in order to expel the arsenic, sulphur, &c.

When the ore contains arsenic, it is well to mix it, after roasting as long as any arsenical fumes are perceptible, with some powdered charcoal, and to heat a second time to bright redness, so as to expel the remainder of the arsenic, as far as possible.

The matt is then to be reduced as in the last case, with black flux and borax. The button of impure copper thus obtained is fused in a bone-ash cupel, placed in a muffle, and a little pure lead added to it. This latter, together with the other more oxidizable metal, is then converted into oxide, which, in a fused state, dissolves the other oxides, and is absorbed, together with these, by the cupel. When the cupellation is terminated, which is known by the sudden brightening of the fused globule, and by the cessation of the rotatory motion which it exhibits during the process, a little vitrified borax is thrown over it; the cupel is then withdrawn, allowed to cool, and the button (which should be perfectly malleable) removed, lightly struck with a hammer, to detach adhering slag, and weighed.

The above is only a general outline of the methods pursued in the assaying of copper-ores. It would be far beyond the scope and intention of this work to enter into the various details of these processes, for which we refer to the technical works on assaying.

BISMUTH.

Sym. Bi. Eq. 213. Sp. Gr. 9.8.

§ 263. This metal is tolerably abundant in the mineral kingdom, where it is generally found in the metallic state.

Preparation.—The bismuth of commerce, the extraction of which will be presently described, contains small quantities of sulphur, arsenic, lead, silver, and other impurities. It may be rendered sufficiently pure for most purposes by fusing it with $\frac{1}{4}$ its weight of nitre, in an earthen crucible, at such a temperature that the salt shall begin to evolve a little oxygen, which will act upon the more oxidizable metals, and upon the sulphur, thus causing these impurities to pass into the slag.

If it is desired to obtain perfectly pure bismuth, the product of the above operation is dissolved in nitric acid, the silver precipitated by hydrochloric acid, the lead by sulphuric acid, and lastly, the teroxide of bismuth by potassa; the precipitate is well washed, and reduced by charcoal.

Properties.—Bismuth has a grayish-white colour, with a tinge of red, and metallic lustre. It is brittle, and very crystalline; it fuses at the low temperature of 476°.5 F. (247° C.), and volatilizes at a considerably higher temperature. Fused bismuth suffers considerable expansion in the act of solidifying. When allowed to cool very slowly, it crystallizes in large rhombohedra, similar to those of common salt, and aggregated, like these latter, into the form of steps; this may be easily seen on breaking the crust as soon as it has formed upon the surface of the fused metal, and pouring out the liquid portion, when a crystallized mass remains in the vessel. The bismuth employed for this experiment should be very pure.

Bismuth is not affected by dry air, but tarnishes if moisture be present; when heated in air, it burns with a bluish flame, giving off yellow fumes of oxide.

This metal decomposes water only at a very high temperature; and does not decompose it at the ordinary temperature in presence of acids.

Nitric acid readily dissolves bismuth, producing nitrate of the teroxide.

Hydrochloric and dilute sulphuric acids have scarcely any action upon bismuth; concentrated sulphuric acid oxidizes and dissolves it with the aid of heat; sulphate of teroxide of bismuth being formed, and sulphurous acid evolved.

BISMUTH AND OXYGEN.

Teroxide of bismuth	BiO_3
Bismuthic acid	BiO_3

§ 264. A *suboxide of bismuth* is also said to be formed when the metal is heated in air to a temperature a little above its fusing-point; it is black, and burns when heated in air, forming teroxide of bismuth. Dilute nitric acid decomposes it into metal and teroxide, the latter dissolving in the acid.

Some chemists estimate the equivalent of bismuth at 106.5, when the first of the above oxides is written Bi_2O_3 , and the second, Bi_2O_5 .

TEROXIDE OF BISMUTH (*sometimes called PROTOXIDE, and sometimes SESQUIOXIDE OF BISMUTH*).

BiO_3 . Eq. 237.

The anhydrous teroxide is formed when bismuth is heated with free access of air; it may also be obtained by heating the basic nitrate of bismuth.

It has a yellow color, is tasteless and inodorous. When heated, it fuses easily, and assumes a brownish color. Fused teroxide of bismuth soon penetrates an earthen crucible, giving rise to a fusible silicate. It is not volatile, and may be easily reduced by carbon or hydrogen at a high temperature.

Teroxide of bismuth combines with acids, forming salts, which have always an acid reaction.

Hydrated teroxide of bismuth, $\text{BiO}_3 \cdot \text{HO}$, is precipitated when a solution of a bismuth-salt is mixed with a slight excess of potassa or ammonia.

It forms a white precipitate, which, when boiled in the supernatant liquid, is converted into a collection of small yellowish needles of the anhydrous teroxide.

NITRATE OF TEROXIDE OF BISMUTH, OR NITRATE OF BISMUTH. $\text{BiO}_3 \cdot 3\text{NO}_3$.

To prepare this salt, bismuth is dissolved in dilute nitric acid, with the aid of heat, and the solution concentrated by evaporation, when it deposits, on cooling, deliquescent four-sided prisms, of the formula $\text{BiO}_3 \cdot 3\text{NO}_3 + 10\text{Aq}$, which are decomposed by exposure for some hours to a temperature of 302° F. (150° C.), leaving $\text{BiO}_3 \cdot \text{NO}_3 + \text{HO}$; at 500° F. (260° C.), the acid and water are completely expelled.

These crystals dissolve very easily in dilute nitric acid, but are decomposed by water into an acid salt, which passes into solution, and a basic salt, which remains undissolved.

This basic salt, which is known as *Bismuthum album, trisnitrate of bismuth, or flake-white*, varies in composition according to the temperature, the quantity of water added, and the length of time for which it is washed, but its general formula might be written $\text{BiO}_3 \cdot \text{NO}_3 + \text{HO}$. The nitric acid may be gradually removed by washing with boiling water.

The basic nitrate of bismuth is occasionally employed in medicine; it is used, moreover, as a cosmetic for whitening the skin, but becomes black under the influence of sulphuretted hydrogen.

SULPHATE OF TEROXIDE OF BISMUTH ($\text{BiO}_2 \cdot 3\text{SO}_3$) is left as a white fusible powder when finely-divided bismuth is heated with concentrated sulphuric acid.

When treated with water, this salt is decomposed, an acid salt being dissolved, while the residue is found to consist of a basic salt, the composition of which is $\text{BiO}_2 \cdot \text{SO}_3 + \text{Aq}$.

An intermediate salt, of the formula $\text{BiO}_2 \cdot 2\text{SO}_3 + 3\text{Aq}$, has also been obtained.

Sulphate of bismuth forms a double-salt with sulphate of potassa, of the formula $\text{BiO}_2 \cdot 3\text{SO}_3 \cdot 3(\text{KO} \cdot \text{SO}_3)$.

A basic carbonate of bismuth, of the formula $\text{BiO}_2 \cdot \text{CO}_2 + \text{Aq}$, is precipitated when carbonate of soda is added to an acid solution of nitrate of bismuth:—¹



From the tendency of teroxide of bismuth to form basic salts, it will be seen that it is a feeble base.

BISMUTHIC ACID, BiO_2 .

This acid is but little known.

It is formed by heating a mixture of teroxide of bismuth with potassa and chlorate of potassa.

In order to prepare it, a current of chlorine may be passed through a very concentrated solution of potassa in which teroxide of bismuth is suspended; the insoluble bismuthate of potassa is thus obtained as a red powder, which is treated with nitric acid to remove the potassa and any excess of teroxide of bismuth, when bismuthic acid is left as a bright red substance which is easily decomposed by heat, leaving an intermediate oxide, which may be represented as $\text{BiO}_2 \cdot \text{BiO}_2$; it is also decomposed when heated with sulphuric acid, sulphate of teroxide of bismuth being produced, and oxygen evolved.

The above-mentioned *intermediate oxide* may be obtained by heating a mixture of potassa and teroxide of bismuth in contact with air; it is a brown substance which evolves oxygen when heated with acids, yielding salts of teroxide of bismuth.

TERCHLORIDE OF BISMUTH, BiCl_3 .

§ 265. *Preparation*.—In order to prepare the terchloride, powdered bismuth may be gently heated in a retort through which a current of dry chlorine is passed, when combination takes place, with great disengagement of heat, and if the temperature be afterwards raised, the terchloride distils over.

It may also be obtained by distilling 1 part of powdered bismuth with 2 parts of chloride of mercury (corrosive sublimate).

When bismuth is dissolved in nitro-hydrochloric acid, or when its oxide is dissolved in hydrochloric acid, and the solution evaporated, hydrated terchloride of bismuth is obtained.

Properties.—The anhydrous terchloride deliquesces in air; it is fusible and volatile; it dissolves in water acidulated with hydrochloric acid, but is decomposed by pure water, a white oxychloride of bismuth being precipitated. A similar crystalline precipitate is formed when a concentrated solution of the terchloride is poured into water, and this reaction is turned to advantage in the detection of bismuth in analysis.

The composition of this oxychloride is $\text{BiCl}_3 \cdot 2\text{BiO}_2 \cdot 6\text{HO}$, and its formation may be represented by the equation:—



¹ If the solution be nearly neutral, the precipitate is anhydrous.

When heated, a part of the terchloride is volatilized, and the residue has the composition $\text{BiCl}_3, 6\text{BiO}_2$.

Terchloride of bismuth forms crystallizable double-salts with the alkaline chlorides.

The above-mentioned hydrated oxychloride of bismuth is sometimes used as a cosmetic, under the name of *pearl-white*. It is prepared for this purpose by pouring an acid solution of nitrate of bismuth into solution of chloride of sodium.

There appear to be two sulphides of bismuth.

Bisulphide of bismuth (BiS_2), is sometimes found native; it may be prepared by the direct combination of its elements, or by fusing the tersulphide with an equal weight of bismuth, when it crystallizes on cooling, and the excess of metal may be decanted.

Tersulphide of bismuth (BiS_3), occurs in the mineral kingdom as *bismuth-glance*; it has a gray color and metallic lustre; its crystals are prismatic, and it is therefore isomorphous with the tersulphide of antimony.

The tersulphide of bismuth fuses when heated, and, with access of air, is converted into teroxide, sulphurous acid being evolved.

When sulphuretted hydrogen is passed through a solution of a salt of bismuth, a black precipitate of tersulphide of bismuth is obtained. This precipitate is insoluble in the alkaline sulphides, and in dilute sulphuric acid; it dissolves very sparingly in hydrochloric acid, but readily in nitric.

METALLURGY OF BISMUTH.

§ 266. The chief forms in which bismuth occurs in nature are the following:—

Native bismuth.

Teroxide of bismuth, which forms a very rare mineral known as *bismuth-ochre*.

Carbonate of bismuth.

Bisulphide of bismuth.

Tersulphide of bismuth, which is often associated with the sulphides of lead, copper, and silver.

Arsenide of bismuth.

Silicate of bismuth, or bismuth-blende.

Bismuth is always extracted from the ores which contain it in the state of metal. These are introduced into cast-iron cylinders placed in an inclined position across a furnace; the upper end of the cylinder is closed, and the lower only partially so, by a plate pierced with a hole which allows the bismuth to flow into a receptacle placed beneath; the cylinders are moderately heated, when the metal fuses, and is thus separated from the earthy matters with which it was surrounded.

The uses of bismuth are very limited.

It forms certain alloys which are remarkable for their great fusibility.

An alloy of 8 bismuth, 5 lead, and 3 tin is known as *Newton's fusible alloy*, and is employed for taking moulds, &c. This alloy fuses at about 203°F . (95C .), although the most fusible of its constituents requires a much higher temperature.

The fusibility of these alloys may be varied to almost any extent by altering the proportions of their ingredients; they are sometimes employed in the construction of the safety-valves of steam engines, which fuse, and allow the egress of steam when the pressure (and, therefore, the temperature) has attained a certain point; but since the alloy, when heated for some time, is capable of separating into a less fusible compound and one that is more fusible, these valves have been found unsafe. Bismuth enters into the composition of some kinds of *pevter*; it is also employed in *type-metal*, where its property of expanding during solidification causes it to enter the very finest parts of the mould.

For the analysis of Newton's fusible alloy, see *Quantitative Analysis, Special Methods*.

Assay of Ores of Bismuth.—Ores of this metal are assayed by fusion, at a moderate heat, with considerable quantities of borax and black flux. The button is extracted in the usual manner, and weighed.

GOLD.

Sym. Au. Eq. 197.¹ Sp. Gr. 19.3.

§ 267. *Preparation of Pure Gold.*—Standard gold is alloyed with copper and silver; in order to purify it, we may dissolve it in a mixture of 1 part of nitric and 4 parts of hydrochloric acid, which leaves the silver as insoluble chloride. The solution is diluted and filtered, the filtered liquid carefully evaporated almost to dryness, to expel excess of acid; water is then added, and the solution boiled with solution of sulphate of iron; the precipitated gold (in the form of a dark purple powder) is heated with hydrochloric acid, and subsequently well washed with water; if great care be taken to expel excess of acid, oxalic acid may be advantageously substituted for the iron-salt, since the gold is then precipitated in large flakes, which cohere readily, and may easily be washed.

Properties.—Gold, in its ordinary form, has a reddish-yellow color and metallic lustre, which may be greatly improved by burnishing; it is capable of crystallizing in forms derived from the cube, and is often found in nature in well-defined crystals.

When very much extended, gold transmits a green light; in very fine powder, it is bluish-purple by transmitted, and brown-red by reflected light.

The spec. grav. of fused gold is 19.26, that of hammered gold, 19.37.

Gold is almost as soft as lead; it is the most malleable and ductile of metals, insomuch that it may be beaten into leaves of $\frac{1}{1000}$ of an inch in thickness, one grain of the metal being made to cover $56\frac{1}{2}$ square inches.

The tenacity of gold is inferior to that of iron, copper, platinum, and silver, for a wire $\frac{1}{16}$ inch in diameter will only support 191 lbs.

The fusion of gold requires a very strong white heat, and its conversion into vapor cannot be exhibited in any furnace, but is very perceptible when the metal is held in the focus of a powerful burning glass, or in the oxyhydrogen blowpipe-flame, or placed between the charcoal points of a galvanic battery.

Gold suffers greater contraction in solidifying than any other metal. It undergoes no change by exposure to air, even in the fused state. Like iron, gold is capable of being welded at a high temperature; indeed, even at ordinary temperatures, precipitated gold can be made, by pressure, to cohere into a malleable mass.

Gold does not combine directly with any of the non-metallic elements except chlorine, bromine, fluorine, and phosphorus. It does not decompose water under any circumstances.

Neither sulphuric, hydrochloric, nor nitric acid will act upon gold, but a mixture of hydrochloric acid with any substance (such as nitric acid, chromic acid, binoxide of manganese) capable of oxidizing its hydrogen, will readily dissolve it in the form of chloride; selenic acid oxidizes gold, being converted into selenious acid.

The hydrated alkalis do not act upon gold, even when fused with it, unless air have access, when the gold is converted into auric acid, which combines with the alkali.

The higher alkaline sulphides dissolve this metal in the form of tersulphide.

¹ The equivalent of gold is often represented by $\frac{197}{2} = 98.5$, in which case the two oxides become Au_2O and Au_2O_3 , and so on for the corresponding chlorides, &c.

GOLD AND OXYGEN.

(Prot-) oxide of gold AuO.
 Teroxide AuO₃.

Neither of these is capable of combining with the oxygen-acids.

OXIDE OR PROTOXIDE OF GOLD, AuO.

§ 268. This oxide is precipitated as a violet-colored powder, when the (proto-) chloride of gold is decomposed by a dilute solution of potassa.

It is easily decomposed by heat, and is not affected by oxygen-acids; hydrochloric acid decomposes it, forming terchloride of gold, a portion of the metal being separated:—



This oxide is soluble in alkalis only at the moment of precipitation:¹

Although oxide of gold does not combine directly with oxygen-acids, a salt has been obtained which is regarded as a compound of the hyposulphite of soda with hyposulphite of oxide of gold, $\text{AuO.S}_2\text{O}_3.3(\text{NaO.S}_2\text{O}_3).4\text{Aq}$.

This salt has been obtained in white needles, by mixing dilute solutions of terchloride of gold and hyposulphite of soda, and adding alcohol; it is insoluble in the latter, but readily soluble in water; the solution has a sweet taste. The salt is decomposed by heat into sulphate of soda and metallic gold. Nitric acid also causes a separation of metal. It is worthy of remark that the properties of the oxide of gold and of the hyposulphurous acid have suffered considerable alteration in this combination; thus, sulphate of iron, chloride of tin, and oxalic acid do not reduce the gold; again, no deposition of sulphur, or evolution of sulphurous acid is observed on mixing the solution with dilute sulphuric acid. When the solution is treated with chloride of barium, a gelatinous precipitate, containing barium in place of sodium, is formed.

A solution of the soda-salt is employed for fixing the pictures obtained by the Daguerreotype process.

PURPLE OF CASSIUS, $\text{AuO.SnO}_2.\text{SnO.SnO}_2 + 4\text{HO}$.

Preparation.—Several methods have been proposed for the preparation of this substance.

I. The best process for obtaining it in the pure state is said to be the following: 310 grs. of gold are dissolved in 1550 grs. of *aqua regia*, consisting of 1 part of commercial nitric, and 4 parts of commercial hydrochloric acid; the solution is evaporated to dryness on a water-bath, the residue dissolved in water, the solution filtered, diluted with 20 or 30 ounces of water, and placed in contact with granulated tin; the purple precipitate is washed, and dried at a gentle heat.

II. 1 part of granulated tin is dissolved in hydrochloric acid; 2 other parts of tin are dissolved in a mixture of 3 parts of nitric and 1 part of hydrochloric acid; 7 parts of gold are dissolved in *aqua regia*, composed of 1 part of nitric and 6 parts of hydrochloric acid; this last solution is diluted with a considerable quantity of water, and mixed with the solution of tin in *aqua regia* (bichloride of tin); to the mixed solution, that of (proto-) chloride of tin is added, drop by drop, till the precipitate has a fine purple color; an excess of this reagent renders it brown.

¹ According to the recent experiments of Fremy, this oxide is decomposed by alkalis into metallic gold and auric acid, which combines with the alkali.

III. An alloy is made by fusing together 1 part of gold, $\frac{1}{2}$ part of tin, and 4 or 5 parts of silver; this alloy is treated with nitric acid, which dissolves the silver, leaving the gold and tin in an oxidized state as a purple residue.

Properties.—The nature of purple of Cassius has been the subject of much discussion, but the formula given above explains most of the reactions exhibited by this compound.

Purple of Cassius, when heated, evolves water only, leaving a residue which consists of 1 eq. gold, and 2 eqs. binoxide of tin. When freshly precipitated, purple of Cassius dissolves in ammonia, but the solution is decomposed by exposure to light, becoming blue, and finally colorless, metallic gold being precipitated, whilst binoxide of tin remains in solution. It is decomposed by hydrochloric acid, bichloride of tin being formed, and metallic gold left.

The purple of Cassius is employed for imparting a purple-red color to glass and porcelain.

TEROXIDE OF GOLD, AURIC ACID, AuO_3 .

In order to prepare this oxide, a solution of terchloride of gold is heated with pure magnesia, and the mixture of magnesia and aurate of magnesia thus obtained, boiled with nitric acid, which dissolves the magnesia, leaving hydrated auric acid.¹

This substance has a yellow or brown color; it is reduced when exposed to light; the water is easily expelled by a gentle heat, anhydrous auric acid being left; at a higher temperature, this last is decomposed into its elements. Auric acid is insoluble in water, but dissolves in hydrochloric acid:—



It also dissolves, to some extent, in sulphuric, nitric, and acetic acids, but is precipitated from these solutions by water; it is soluble in solutions of potassa and soda. This oxide is very easily reduced to the metallic state by hydrogen or carbon, with the aid of a gentle heat; alcohol and most other organic substances also separate metallic gold.

The hydrate of auric acid is obtained by carefully neutralizing solution of terchloride of gold with potassa.

Aurate of potassa is prepared by dissolving auric acid in solution of potassa, and evaporating *in vacuo*. The salt crystallizes in yellow tufts, the formula of which is $\text{KO} \cdot \text{AuO}_3 + 6\text{Aq}$. It is easily decomposed by heat, leaving a residue of peroxide of potassium and metallic gold. Aurate of potassa is very soluble in water; the solution is yellow, has an alkaline reaction, and is very easily reduced. This salt may be used for electro-gilding.

Aurate of soda resembles the potassa-salt.

Aurate of ammonia is not known; when auric acid is digested with solution of ammonia, a gray compound is obtained, the formula of which is said to be $\text{AuO}_3 \cdot 2\text{NH}_3 \cdot \text{HO}$; this compound is known as *fulminating gold*, since it explodes with great violence when rubbed, or gently heated, and often spontaneously.²

The alkaline aurates yield, with the salts of various metals, precipitates of aurates, which are mostly soluble in excess of the precipitants.

A compound, in which the teroxide of gold appears to play the part of a base is precipitated when sulphite of potassa is added to a solution of the aurate; it forms long silky needles, of the composition $\text{AuO}_3 \cdot 3\text{SO}_3 \cdot 5(\text{KO} \cdot \text{SO}_3) + 5\text{Aq}$.

This compound is sometimes called *aurosulphite of potassa*.³ Its solution

¹ A better process consists in boiling terchloride of gold with potassa until the color has almost disappeared, precipitating by sulphuric acid, and purifying the teroxide thus obtained by dissolving in nitric acid, and precipitating by water.

² Another fulminating compound of gold exists, and is described at page 398.

³ Since the reactions of teroxide of gold are to some extent masked in this combination,

yields a fine coherent deposit of gold when heated, and decomposes after a time when kept.

An intermediate oxide of gold, having the composition AuO_2 , is said by some to be produced, when chloride of tin, and certain organic substances, act upon terchloride of gold.

An oxide of the formula AuO_3 , has been pointed out by Figuier.

CHLORIDE, OR PROTOCHLORIDE, OF GOLD, AuCl .

§ 269. This chloride is prepared by heating the terchloride to about 392°F . (200°C .); it is then obtained as a pale yellow insoluble substance, easily decomposed, by the action of light or heat, into metallic gold, and the terchloride.

TERCHLORIDE OF GOLD, AuCl_3 .

When gold is dissolved in *aqua regia* (one part nitric, and four parts hydrochloric acid), and the solution carefully evaporated on a water-bath, a red-brown, deliquescent, crystalline mass of the terchloride is obtained. This compound is decomposed by heat, evolving chlorine, and leaving (proto-) chloride of gold, or metallic gold, according to the temperature.

The terchloride is very readily soluble in water and alcohol; its solution is yellow, has an acid reaction, and stains the skin of a purple color, due to reduction. Ether, however, dissolves it most readily; for, if an aqueous solution be shaken with ether, the latter abstracts the whole of the salt, and forms a yellow layer upon the surface of the colorless aqueous liquid; the ethereal solution is called *aurum potabile*, and has been used medicinally; it deposits metallic gold when kept for some time.

Terchloride of gold is easily reduced, even by feeble deoxidizing agents; thus hydrogen, carbon, carbonic oxide, binoxide of nitrogen, phosphorus, sulphurous and phosphorous acids and their salts, terchloride of antimony, the proto-salts of iron, nearly all the metals, most organic substances, and especially oxalic acid, precipitate metallic gold from a solution of the terchloride.

The alkalis and their carbonates decompose terchloride of gold, giving rise to alkaline aurates, and to chlorides of the alkali-metals; the alkaline aurates remain in solution, and yield a precipitate of auric acid upon addition of a stronger acid. The action of potassa upon terchloride of gold may be expressed by the equation:—



Terchloride of gold combines with hydrochloric acid to form a hydrochlorate, which is deposited in golden-yellow prisms, when the mixed solutions are allowed to evaporate spontaneously.

Terchloride of gold is capable of forming very definite crystallizable salts with the hydrochlorates of organic bases, and since these compounds always leave metallic gold upon ignition, their analysis may be effected with great precision, and the high atomic weight of gold enables us to ascertain very correctly, from the amount of this metal, the equivalent of the alkaloid contained in the double-salt.

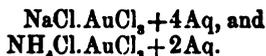
The terchloride is capable of combining with many other chlorides to produce double-salts, which are generally well crystallized, and much more stable than the terchloride itself.

The *aurchloride of potassium*, as it is commonly called, crystallizes in yellow prisms or tables, of the composition $\text{KCl} \cdot \text{AuCl}_3 + 5\text{Aq}$; it is decomposed by

Fremy suggests that it may be regarded as $\text{KO} \cdot \text{AuO}_3 \cdot 4(\text{KO} \cdot 2\text{SO}_3) + 5\text{Aq}$. This salt must be preserved in alkaline liquids, since it is decomposed by pure water, sulphurous acid being evolved, and metallic gold deposited.

heat, evolving chlorine, and leaving a compound of chloride of potassium and (proto-) chloride of gold.

The corresponding sodium and ammonium salts have the formulæ respectively:—



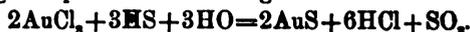
Tetrachloride of gold and some of its double salts are occasionally employed in medicine.

When tetrachloride of gold is digested with an excess of ammonia, a powerful fulminating compound is obtained, the constitution of which is uncertain; it contains gold, chlorine, nitrogen, hydrogen, and oxygen.

SULPHIDES OF GOLD.

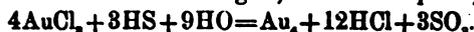
The sulphides of gold are but little known, but they appear to correspond to the oxides.

(Proto-) sulphide of gold is obtained as a dark brown precipitate, when sulphuretted hydrogen is passed into a boiling solution of the tetrachloride:—¹



When a cold dilute solution of tetrachloride is employed, a black precipitate of tersulphide of gold (AuS_2) is obtained; this tersulphide is a sulphur acid; it dissolves (though not very readily) in solutions of alkaline sulphides, and is even capable of expelling the hydrosulphuric acid from the hydrosulphates of alkaline sulphides.

According to Levol, the precipitate obtained by passing sulphuretted hydrogen into a boiling solution of tetrachloride of gold, is not the sulphide, but the metal:—



When a cold solution is employed, the precipitate has the formula $\text{AuS} + \text{AuS}_2$.

METALLURGY OF GOLD.

§ 270. Gold is always found in the metallic state, generally alloyed with other metals, especially with silver and tellurium.²

It occurs sometimes in veins, most commonly associated with quartz; these veins often contain iron-pyrites, and ores of copper, lead, silver, &c.

When the rocks which are traversed by such veins are disintegrated and swept away by torrents and rivers, the heavy particles of gold are deposited, together with part of the quartz, forming an auriferous sand, more or less rich in the precious metal (*alluvial gold*).

Native gold is generally found either in scales, or crystallized in cubes and octohedra, or forms derived from these. Nodules of gold of large size are also sometimes found.

This metal is found in considerable quantity in veins of sulphide of silver, in Mexico, Peru, and the Uralian mountains in Siberia. Sand very rich in gold is found in the beds of streams in Brazil and Africa; alluvial gold is also met with in very minute quantity in some European rivers, especially in France. The recent discoveries of this metal, both in the massive and disseminated states,³ in California and Australia, are well known to all.

¹ Double compounds of sulphide of gold with the sulphides of potassium and sodium have been obtained.

² A native amalgam of gold has also been met with.

³ From 7 to 9 per cent. of silver has been found in the gold-dust from California.

Gold cannot justly be termed a rare metal, for it is very extensively diffused over the surface of the earth, though in small quantities.

EXTRACTION OF GOLD.—The alluvial gold is readily separated from the sand by a process of washing; the arrangements for this purpose differ in different countries, but all proceed upon the principle of washing away the earthy impurities, and leaving the heavier particles of gold; when the grains of gold are mixed with those of platinum (as is sometimes the case), they are shaken with mercury, which dissolves only the gold, to be afterwards separated by distillation.

The gold obtained by washing is known in commerce as *gold-dust*.

The extraction of gold from rocky ores is effected either by fusion, by washing, or by amalgamation.

The process of *fusion* consists in extracting the metal with which the gold happens to be associated (lead, copper, &c.), and separating the gold from the alloy thus obtained (which contains the whole of that metal) by cupellation, which will be described in the section upon lead, or by amalgamation, a process to be presently noticed.

The *washing* of gold-ores depends upon the same principle as the extraction of alluvial gold.

The extraction of gold by *amalgamation* is carried out especially with auriferous pyrites. The mineral is well agitated in a sort of mill, with mercury, a stream of water being at the same time employed to wash away the earthy impurities; the gold and silver, if any be present, dissolve in the mercury, forming a solid amalgam, which is collected on a chamois leather, in order to separate it from the excess of mercury, and distilled, when an alloy of gold and silver remains, which is subjected to the refining process.

REFINING OF GOLD.—It is frequently necessary in practice to separate this metal from silver and copper; this is the case in working the American ores of silver, and in the separation of gold from old coins. The process applied to separating gold and silver is termed the *parting of gold*.

The alloy is granulated by being poured, in a fused state, into water; it is then boiled in a vessel of platinum or of cast iron, with concentrated sulphuric acid; the copper and silver are thus oxidized, and dissolved as sulphates, sulphurous acid being evolved, which is often conducted into leaden chambers, and reconverted into oil of vitriol.¹

The residual gold still contains silver, and must be again treated with sulphuric acid, well washed, and fused.

In order to separate the silver and copper, the solution containing the two sulphates is heated with metallic copper, which precipitates the whole of the silver in a spongy state, to be afterwards washed, dried, and fused.

The solution of sulphate of copper is evaporated to crystallization, and the acid mother-liquors are made use of to economize the sulphuric acid in a fresh refining process.

For the complete success of this process it is necessary that the alloy should not contain more than 20 per cent. of gold, nor more than 10 per cent. of copper. If it be too rich in gold, it is fused with a quantity of auriferous silver.

Alloys poor in gold and silver are submitted to a preliminary roasting, and afterwards treated with dilute sulphuric acid, which dissolves the oxide of copper, leaving an alloy sufficiently rich to be refined in the ordinary way.

¹ The extraction of the silver proceeds rapidly at first, but afterwards very slowly, and is never, according to Pettenkoffer, absolutely perfect. This chemist recommends fusion with bisulphate of soda for the complete purification of the gold.

Moreover, the residual metal contains traces of sulphate of lead, and basic sulphate of iron, from which it may be freed by treatment, first with carbonate of soda, and afterwards with nitric acid.

By this process, gold may be economically extracted from alloys containing only 0.05 per cent. of this metal.

The refined gold has a degree of purity represented by the fraction $\frac{995}{1000}$, which indicates that 1000 parts of metal contain 995 of gold.

The purification may be carried still farther, by fusing the metal with three times its weight of silver, and boiling the alloy with nitric acid, which leaves the gold undissolved (*quartation*).

Perfectly pure gold is far too soft to be employed for the fabrication of coins, vessels, ornaments, &c.

Gold for coin is alloyed with 1 part of copper to 11 parts of pure gold.

Jewellers' gold, for ornamental purposes, is an alloy containing 3 parts of gold to 1 of copper.

These alloys also contain a small quantity of silver.

Goldleaf, is made by rolling out a bar of pure gold to a long ribbon, which is then cut up into squares, and extended by beating, between layers of fine vellum, with a heavy hammer; the thin squares are then subjected to a second beating, between layers of *goldbeater's-skin* (prepared from the intestines of the ox), till they have acquired the requisite degree of extension; in this way, an ounce of gold may be spread over a surface of 100 square feet. But the division of gold is carried still further in the manufacture of the gold-thread used in embroidery; a cylinder of silver is covered with a quantity of goldleaf, amounting to about $\frac{1}{8}$ of its weight; it is then drawn through holes in iron plates till it is reduced to a wire as thin as a hair; 6 ounces of gold may thus extend over a wire above 200 miles in length, and yet, if this wire be dipped in nitric acid, the silver is dissolved out, and a hollow cylinder of gold remains.

Gold combines directly with almost all other metals.

Copper imparts a deeper color to gold, renders it harder and more fusible, but diminishes its malleability and ductility.

The *alloys of gold and copper* have a lower specific gravity than would be expected in a mere mixture of the two metals. A minute quantity of lead is capable of injuring the malleability of these alloys. Alloys of copper and gold, being more fusible than the latter metal, are employed for soldering pieces of gold together.

GILDING.—In order to gild glass or porcelain, goldleaf is powdered and mixed with oil of turpentine and borax; the mixture is painted on the ware, which is then strongly heated in a muffle.

Wood, plaster, &c., are covered with goldleaf, by the intervention of some adhesive substance (size, varnish, &c.).

Metals are covered with gold either by the use of an amalgam, or by mere immersion in a solution of gold, or by the electrotype process.

The amalgam of gold is prepared by dissolving gold-leaf in mercury, with the aid of heat, and separating the excess of mercury from the semi-solid amalgam by pressure.

The articles to be coated with gold, having been perfectly cleaned, are amalgamated by rubbing them with a brush which has been dipped into a solution of nitrate of mercury, and covered with the amalgam; they are then heated, to expel the mercury, and burnished.

The gilding of copper ornaments is sometimes effected by immersing them in a boiling solution of an alkaline aurate, prepared by mixing tetrachloride of gold with an excess of an alkaline carbonate.

The process of *electro-gilding* consists in decomposing a solution of gold by a galvanic current, in such a manner that the metal shall be deposited upon the objects to be gilt. A solution of tetrachloride of gold in cyanide of potassium is generally employed; this is placed in a wooden vessel, varnished interiorly, and the articles to be operated upon are suspended in it: these are connected with the

negative (copper) pole of the battery, whilst the positive (amalgamated zinc) pole communicates with a plate of gold suspended in the solution, and intended to dissolve, and thus to replace, the gold deposited.

Copper and its alloys, as well as iron, steel, and tin, may be gilt in this way, provided that the last three are first covered with a film of copper, for which purpose they are immersed in a solution of cyanide of copper in cyanide of potassium.

§ 271. ASSAY OF ALLOYS OF GOLD.—For practical purposes, the value of alloys of gold is often estimated by means of the *touchstone*. This is a hard black stone, originally brought from Lydia, but now obtained from Silesia; the Silesian touchstone is a species of basalt.

The alloy to be examined is rubbed upon this stone, when it leaves a streak varying in appearance according to the composition of the alloy; the first few streaks are unnoticed, since most alloys are improved in color by refining the gold at the surface; by comparing the streaks left upon the stone with those produced by auriferous alloys of known composition, the operator is enabled, after a little experience, to judge, approximatively, of the proportion of gold; this is rendered still easier by moistening the streaks with a mixture of 98 parts of nitric acid of sp. gr. 1.34 and 2 parts of hydrochloric of 1.17, which readily dissolves the copper, but not gold; the effect of the acid upon the streaks is compared with that upon streaks made by the standard alloys.

In experienced hands this mode of testing gives results which are correct within 1 per cent.

Assay of Alloys of Gold by Cupellation.—The only alloys of gold, the assay of which is of practical importance, are those containing silver or copper, or both. The amount of gold existing in the alloy is first roughly ascertained by means of the touchstone; 7 or 8 grs. of the alloy are then fused, upon a cupel made of bone-ash, and placed in a muffle, with so much silver (accurately weighed) as, together with the silver previously existing in the alloy, will give a proportion of 8 or 4 parts for 1 part of gold; in addition, a quantity of pure lead is employed equal to about 3 or 4 times that of the gold and silver; the lead is first introduced into the heated cupel, and when it is in complete fusion, the gold and silver are thrown in, wrapped up together in a piece of paper.

When the cupellation is finished, which the operator recognizes by the clear appearance and tranquil state of the metallic button, the latter is allowed to cool, and its weight carefully determined; by subtracting this weight from that of the alloy and silver originally employed, the amount of copper is ascertained.

The alloy of gold and silver is now annealed and beaten into a thin plate, which is rolled up and heated in a flask with moderately dilute nitric acid; when this ceases to act it is decanted, and the *cornet* (as it is termed) is boiled with a more concentrated acid; it is afterwards washed with water till the washings are no longer rendered turbid by hydrochloric acid; the flask is then filled with water, closed with the thumb, and carefully inverted into a crucible filled with water, so that the cornet may fall into the crucible, where it is dried, ignited, and afterwards weighed; its weight, subtracted from that of the original cornet, gives that of the silver.

The first of these operations, where the gold is alloyed with three parts of silver, is known as *quartation*, while the separation of the two metals by nitric acid is termed *parting*.

The theory of the cupellation is very simple; the copper and lead are oxidized by the current of air passing through the muffle, and the suboxide of copper is dissolved by the fused oxide of lead (litharge), and absorbed by the bone-ash cupel; whilst the gold and silver remain untouched.

If there were less silver than amounted to three times the weight of the gold, the parting by nitric acid would not be complete, whereas, if considerably more

silver were employed, the gold would be left in a very finely divided state, and could not readily be weighed.

This process, though not absolutely correct, is sufficiently so for all commercial purposes.

For the analysis of alloys of gold, silver, and copper, see Quantitative Analysis, Special Methods.

The quantity of gold contained in auriferous sand may be determined roughly by washing a large quantity, and weighing the residual gold, but more accurately by extracting the metal with nitro-hydrochloric acid, and reducing the gold with oxalic acid, with the precautions mentioned above.

Assay of Auriferous Ores.—If the ore to be examined contains oxide of lead, it is only necessary to fuse it in an earthen crucible with a sufficient quantity of black flux.

If the ore contain no oxide of lead, it should be fused with a mixture of litharge and black flux.

* When considerable quantities of deoxidizing agents are present, such as pyrites, &c., litharge only may be used.

Sometimes, when the quantity of reducing minerals present is very large, so that too much lead would be reduced if enough litharge were added to oxidize and remove the whole of the sulphur, a little nitre is added, together with the litharge.

If 400 grains of ore are employed, they should be mixed with about an equal weight of litharge, and about 300 grains of black flux.

The button of lead obtained should never weigh more than 200 grains.

The fusion is conducted in a wind furnace. The button, which consists of lead, silver, gold, copper, &c., is then cupelled and parted as in the analysis of alloys of gold (p. 401).

When the amount of gold is required in a mixture of gold and quartz free from other minerals, it may be very readily calculated from the specific gravities of the constituents as compared with that of the mixture. If possible, a piece of pure quartz may be separated from the mass, and its actual specific gravity determined; but if this cannot be done, the number 2.6 may be taken as sufficiently accurate for practical purposes.

The calculation is effected as follows:—

Let m = specific gravity of the gold.
 “ n = “ “ quartz.
 “ p = “ “ mixture.
 “ x = weight of gold per cent.

Then $100 - x$ = weight of quartz per cent.

$\frac{x}{m}$ = volume of gold in 100 parts by weight.

$\frac{100 - x}{n}$ = volume of quartz “ “

$\frac{100}{p}$ = volume of 100 parts, by weight, of the mixture.

$\frac{x}{m} + \frac{100 - x}{n} = \frac{100}{p}$

$mpx + 100 mp - mpx = 100 mn$

$(np - mp)x = 100(mn - mp)$

$x = \frac{100(mn - mp)}{np - mp}$

A result expressed by saying that the quantity of gold per cent. in a mixture of gold and quartz, is the quotient obtained by dividing, by the difference of the

products of the specific gravities of gold and quartz multiplied with that of the mixture, 100 times the difference between the products of the specific gravity of gold into that of quartz, and of the specific gravity of gold into that of the mixture.

 PLATINUM.

Sym. Pt. Eq. 98.7. Sp. Gr. 21.5.

§ 272. This somewhat rare metal was not applied to any useful purpose before the commencement of the present century. Its name is derived from the Spanish word *platina*, signifying little silver.

Preparation.—The extraction of this metal from its ores will be described hereafter; the platinum of commerce is nearly pure, containing merely a little iridium, which renders it harder, but somewhat less malleable than pure platinum; in order to purify the ordinary metal, it is dissolved in nitro-hydrochloric acid, the solution evaporated to expel excess of acid, the residue redissolved in water, and mixed with solution of chloride of potassium, which produces a yellow crystalline precipitate containing the double chlorides of platinum and potassium, and of iridium and potassium. This is dried, mixed with carbonate of potassa, and heated to redness in an earthen crucible; the bichloride of platinum is decomposed according to the equation:—



the iridium is converted into oxide, which is left behind, together with the platinum, when the fused mass is washed with water; this residue is heated with dilute nitro-hydrochloric acid, which dissolves only the platinum; the solution is mixed with chloride of ammonium, and the platinum thus precipitated as a double chloride of platinum and ammonium, which may be washed and heated to redness, when the chloride of ammonium and chlorine are expelled, and the metal left as a spongy mass, the conversion of which into malleable platinum will be presently described.

Properties—Platinum is a nearly white metal, capable of a high lustre; it is the heaviest substance known, its specific gravity being 21.5. It is very malleable and ductile, standing next to gold and silver with respect to the latter quality. Platinum is remarkable for its tenacity, in which it is only surpassed by iron and copper. A wire of this metal, of $\frac{1}{16}$ inch in diameter, will sustain a weight of 361 lbs.

Platinum is rather a soft metal; it is harder than copper, but not so hard as silver. It is less expansive by heat than any other metal, and conducts it very slowly. Platinum is employed in three different forms, viz., *malleable platinum*, *spongy platinum*, and *platinum-black*, which is in an extremely divided state. We have already mentioned that spongy platinum is obtained by igniting the double chloride of platinum and ammonium. The preparation of platinum-black will be presently described.

In either of these forms, platinum possesses the remarkable property of condensing gases in its pores, and thus seeming to absorb a certain quantity of them; even malleable platinum exhibits this property in a high degree; hence, a perfectly clean plate of this metal is capable of inducing the combination of hydrogen and oxygen at a comparatively low temperature. This property may also be exhibited by suspending a helix of platinum-wire in the flame of a spirit-lamp, which is allowed to heat the wire to redness, and then suddenly blown out; the

wire will then continue for any length of time at a red heat, in consequence of the energetic combination of the vapor of alcohol with the atmospheric oxygen induced by the peculiar surface-action of the metal. In this case the alcohol is not completely burnt; acrid odors, due to the imperfect oxidation of this body, are evolved. The experiment is even more satisfactory when a platinum crucible is heated to bright redness in the flame of a gauze gas-burner, and the gas extinguished, and rapidly turned on again, when the cold stream of gas will maintain the temperature of the crucible.

This interesting property of platinum will be reverted to in the description of platinum-black.

Platinum is not in the least affected by exposure to air, even at high temperatures; it is very infusible, and does not undergo a change of state in the hottest furnaces; it may, however, be easily fused in the oxyhydrogen blowpipe-flame, or between the charcoal points of a powerful galvanic battery. A platinum wire, held in the flame of the oxyhydrogen blowpipe, emits brilliant white sparks (due to the combustion of the metal?). A very high temperature appears to volatilize it slightly.

Platinum is very easily welded, especially at a high temperature.

This metal, like gold, is unalterable by many chemical agents, and hence is largely employed in the forms of crucibles, spatulas, dishes, wire, and foil, in chemical operations; since, however, it is very costly, it is necessary that the chemist be fully acquainted with the circumstances under which platinum vessels are acted upon, in order that he may avoid accidents.

Platinum does not decompose water under any circumstances; it is not attacked by nitric, hydrochloric, or sulphuric acid; but a mixture of nitric and hydrochloric acids dissolves it in the form of bichloride. Potassa and soda, in the fused state, act upon platinum, probably in the same way as upon gold, by inducing the action of the oxygen of the air upon the metal.

Lithia acts upon platinum much more rapidly than the above alkalis.

A mixture of potassa and nitrate of potassa (which is produced by the action of heat upon the latter), attacks this metal very readily.

Several other oxides, which are not reduced by heat, also affect platinum.

Chlorine slowly attacks platinum; iodine and bromine have no effect upon it. In the nascent state, however, these elements are capable of acting upon the metal.

Fluorine appears to combine readily with platinum.

Malleable platinum is scarcely affected by sulphur, even at a high temperature; spongy platinum, however, combines with it.

Phosphorus and arsenic act upon platinum at a high temperature, forming a very fusible phosphide, or arsenide; hence, substances containing phosphorus in an unoxidized state (brain, blood, &c.), should never be burnt in a crucible of this metal, neither should phosphates be heated in contact with reducing agents in a platinum crucible.

Silicon in the nascent state converts platinum into a brittle silicide; hence, silicic acid and carbon should never be allowed to come simultaneously in contact with platinum at a high temperature; for this reason, platinum vessels are never directly heated by a coal, coke, or charcoal fire, but are imbedded in a layer of magnesia, and inclosed in a Hessian crucible.

Most metals are capable of combining directly with platinum, if the temperature be sufficiently high, so that we should avoid the contact of this metal with easily reducible metallic oxides in the presence of reducing agents (filter-paper, for instance).

When platinum is alloyed with silver, it becomes soluble in nitric acid; this is often cited as an example of catalytic action.

Platinum-black.—This form of platinum, which derives importance from the

interesting processes of oxidation which it is capable of inducing, may be prepared by several methods:—

I. (Proto-) chloride of platinum is dissolved in a concentrated solution of potassa, with the aid of heat, and alcohol is added, by degrees, with constant stirring, to the hot liquid; the platinum is precipitated as a black powder, which is boiled, successively, with alcohol, hydrochloric acid, potassa, and water.

II. A solution of bichloride of platinum is boiled, with constant agitation, with carbonate of soda and sugar, when the sodium takes the chlorine of the bichloride of platinum, and the metal is precipitated, the oxygen of the soda serving to convert the carbon and hydrogen of the sugar into carbonic acid and water.

III. By boiling a solution of (proto-) sulphate of platinum with alcohol.

By whichever method the platinum-black is prepared, it must be very carefully washed, and dried between blotting-paper.

It will be remembered that when platinum-black (or spongy platinum) is thrown into a mixture of hydrogen and oxygen, it causes combination, attended by explosion, and that a jet of hydrogen may be inflamed by directing it upon platinum in one of these states, air being present (*see* p. 119).

If a mixture of sulphurous acid and oxygen be passed over platinum-black, or sponge, anhydrous sulphuric acid is produced.

A mixture of binoxide of nitrogen, or ammonia, with an excess of oxygen, passed over heated spongy platinum, or platinum-black, gives rise to nitric acid:—



On the other hand, the oxides of nitrogen, when mixed with an excess of hydrogen, and exposed to the action of the heated platinum, yield ammonia and water:—



Both spongy platinum and platinum-black lose these peculiar properties after some time, but they may be revived by heating with nitric acid, washing with water, drying at a gentle heat, and, in the case of spongy platinum, heating to redness.

PLATINUM AND OXYGEN.

(Prot-) oxide	PtO
Binoxide	PtO ₂

OXIDE OR PROTOXIDE OF PLATINUM.

PtO.

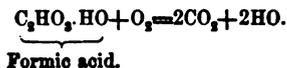
§ 278. This oxide is known only in the form of hydrate, which is obtained, as a black powder, by decomposing the (proto-) chloride of platinum with potassa.

¹ It is in the department of organic chemistry that we find the most interesting examples of the action of platinum-black.

If a drop of alcohol be projected upon a little platinum-black, the latter becomes vividly incandescent, and the excess of alcohol takes fire; again, when platinum-black is placed in a capsule and covered with a bell-jar, the sides of which are wetted with alcohol, the latter is gradually oxidized, and converted into acetic acid:—



Formic acid, moreover, is immediately converted into carbonic acid and water, by contact with platinum-black:—



The hydrated oxide, when freshly precipitated, dissolves in excess of potassa.

If the hydrate be heated, it parts with water and oxygen, leaving metallic platinum; in fact, this oxide is very unstable; most reducing agents decompose it with facility. Oxide of platinum possesses feeble basic characters; it dissolves slowly in sulphuric, nitric, and acetic acids, yielding brown solutions.

When this oxide is heated with hydrochloric acid, the metal is separated, and bichloride of platinum formed:—



The salts of (prot-) oxide of platinum are little known, and, for the most part, do not crystallize; the oxalate has been obtained in copper-red needles by heating hydrated binoxide of platinum with oxalic acid.¹

Solutions of (prot-) oxide of platinum are not precipitated by chloride of ammonium, and may thus be distinguished from those of the binoxide.

BINOXIDE OF PLATINUM, PLATINIC ACID.



Anhydrous binoxide of platinum may be obtained by gently heating the hydrate; it is a black powder, which does not dissolve in acids or alkalies.

The *hydrate* ($\text{PtO}_2 \cdot 2\text{HO}$), is prepared by mixing a solution of bichloride of platinum with an excess of potassa, when a double chloride of platinum and potassium is first precipitated, but redissolves on gently heating, being converted into platinate of potassa; if the solution be now mixed with excess of acetic acid, the hydrated binoxide of platinum is precipitated.

This hydrate forms a red-brown precipitate, somewhat resembling the sesquioxide of iron; when heated, it loses first its water, and then the oxygen. It is easily decomposed by reducing agents.

The hydrate dissolves in acids and alkalies, yielding brown solutions; hence, binoxide of platinum is another example of an oxide which plays, indifferently, the part of a weak base and that of a weak acid.

Fulminating Platinum.—This substance, which is probably a compound of binoxide of platinum with ammonia, is obtained by adding the latter reagent to a solution of sulphate of binoxide of platinum, and digesting the basic double-salt then precipitated, with a dilute solution of soda.

It is a brown powder, insoluble in water, nitric and hydrochloric acids, but soluble in sulphuric acid. It is not exploded by friction or percussion, but detonates violently when heated to about 400° F. (204° C.) Care should therefore be taken, lest it should be formed, unexpectedly, in examining the compounds of platinum.

The *platينات of potassa and soda* may be crystallized; they are decomposed by acids, platinic acid (hydrated binoxide of platinum) being separated.

Nitrate of binoxide of platinum is formed when an alloy of platinum and silver is dissolved in nitric acid; it may be prepared by dissolving the hydrated binoxide in nitric acid, or by decomposing bichloride of platinum with nitrate of silver.

This nitrate does not crystallize; it has a dark-brown color, and leaves metallic platinum when exposed to heat.

Nitrate of binoxide of platinum forms double-salts with the alkaline nitrates.

In order to prepare the *Sulphate of Binoxide of Platinum*, the bisulphide is oxidized with fuming nitric acid, and the liquid evaporated to dryness with a little sulphuric acid. The sulphate has a dark-brown color, and is very soluble

¹ A double salt of the formula $2, \text{PtO} \cdot 2\text{SO}_4 \cdot 3(\text{K}_2\text{O} \cdot \text{SO}_4) \cdot 4\text{5Aq.}$ is deposited as a white precipitate, when the double chloride of platinum and potassium ($\text{KCl} \cdot \text{PtCl}_2$) is heated with sulphide of potassa, and the excess solution concentrated by evaporation.

in water; it does not crystallize. Sulphate of binoxide of platinum combines with the alkaline sulphates to form double-salts.

An *intermediate oxide of platinum* is said to have been obtained by the action of nitric acid on fulminating platinum.

Some chemists assert that a crystalline *compound of platinum with hydrogen* is obtained, when an alloy of platinum and potassium is decomposed by water.

CHLORIDE OR PROTOCHLORIDE OF PLATINUM, PtCl.

§ 274. *Preparation*.—In order to prepare the (proto-) chloride, platinum is dissolved in *aqua regia*, the solution evaporated to dryness, and the residue heated on an oil-bath to about 400° F. (204° C.) as long as any chlorine is disengaged.

This chloride is also precipitated when sulphurous acid is passed through solution of bichloride of platinum not containing an excess of acid:—



Properties.—(Proto-) chloride of platinum has a grayish-green color; it blackens slightly when exposed to light; all the chlorine may be expelled by a high temperature; it is insoluble in water, and in nitric or sulphuric acid, but dissolves in hydrochloric acid, a portion of it being decomposed into metal and bichloride. It dissolves more readily in a solution of bichloride of platinum.

Alkalies decompose the chloride, forming oxide of platinum.

Its solution in hydrochloric acid is not precipitated by chloride of ammonium, but on carefully evaporating the liquid, yellow crystals are obtained, of the formula $\text{PtCl.NH}_4\text{Cl}$.

Similar compounds may be formed with the chlorides of potassium and sodium.

Chloride of platinum, when treated with ammonia, gives rise to several new compounds, the most important of which we shall briefly notice.

AMMONIATED CHLORIDE OF PLATINUM. *Green Salt of Magnus.* PtCl.NH_3 . This compound is formed when (proto-) chloride of platinum is digested for some time with ammonia at a gentle heat. It is, however, more readily prepared as follows: sulphurous acid is passed through solution of bichloride of platinum mixed with excess of hydrochloric acid, until the deep red liquid ceases to precipitate a solution of chloride of ammonium; the solution is then boiled, and ammonia gradually added, when the green salt is precipitated in fine crystalline needles, which are insoluble in water, alcohol, ether, and hydrochloric acid.

When the green compound is heated with an excess of ammonia, it gradually dissolves, and the solution deposits yellowish-white prismatic crystals, of the formula $\text{PtCl}_2.2\text{NH}_3 + \text{HO}$.

This last is known as the *white compound of Reiset*, and should be written $\text{PtN}_3\text{H}_3\text{Cl} + \text{HO}$, since it is the chloride of a new radical,¹ the formula of which is PtN_3H_3 . The water is expelled at 212° F., leaving the anhydrous chloride.

By dissolving the white compound of Reiset in hot water, and decomposing it with sulphate of silver, chloride of silver is precipitated, and the filtered solution, on evaporation, yields colorless crystals, of the formula $\text{PtN}_3\text{H}_3\text{O.SO}_2$; these are the sulphate of a new base, $\text{PtN}_3\text{H}_3\text{O}$, which may be isolated by carefully decomposing the sulphate with baryta-water, filtering, and evaporating the solution *in vacuo*, when white crystals are obtained, of the formula $\text{PtN}_3\text{H}_3\text{O.HO}$.

This hydrated base bears a great analogy to hydrate of potassa; it is deliquescent, has a caustic taste, reacts strongly alkaline to test-papers, and absorbs carbonic acid from the air; it is also capable of expelling ammonia from its salts.

¹ This radical has been recently named *diplosammonium*; the base corresponding to it being termed *diplosamine*.

A pretty complete series of the salts of this base has been obtained.

When it is heated to 230° F. (110° C.), it parts with ammonia and water, and is converted into PtNH_3O (*oxide of platosammonium*), which is a new base, insoluble in water; the *sulphate* of this base has the formula $\text{PtNH}_3\text{O.SO}_2 + \text{HO}$; the *nitrate* is represented by $\text{PtNH}_3\text{O.NO}_2$. These salts are converted into salts of the base $\text{PtN}_2\text{H}_6\text{O}$, when dissolved in ammonia. The *chloride* corresponding to this base, viz. PtNH_3Cl , is isomeric with the green salt of Magnus, and may be obtained by dissolving that compound in a hot solution of nitrate or sulphate of ammonia, when the new salt crystallizes out on cooling.

When the green compound of Magnus (PtCl_2NH_3) is heated with nitric acid, it dissolves, and the solution yields white crystals, which have the formula $\text{PtCl}_2\text{N}_2\text{H}_6\text{O.NO}_2$; in this reaction, 1 equivalent of (proto-) chloride of platinum has been abstracted from the ammoniated chloride, and an equivalent of oxygen added; the compound thus formed is in fact the nitrate of another base (usually termed *Gros's base*, from its discoverer), $\text{PtClN}_2\text{H}_6\text{O}$, which is the oxide of a radical PtClN_2H_6 , isomeric with the chloride of Reiset's radical PtN_2H_6 . Neither the radical nor the base itself has been isolated.

By dissolving the ammoniated (proto-) chloride of platinum in a large excess of nitric acid, two more nitrates are obtained, having the formulæ



The former of these is deposited in needles as the liquid cools, and the latter may be obtained from the mother-liquor.

Other salts of the base, $\text{Pt}_2\text{ClO}_2\text{N}_4\text{H}_{12}$ (*Raewsky's base*) have been obtained.

We have now become acquainted with the three well-defined series exhibited in the subjoined table:—

	Hypothetical Radical.	Base.	Chloride.
Reiset's first base . . .	PtN_2H_6	$(\text{PtN}_2\text{H}_6)\text{O}$	$(\text{PtN}_2\text{H}_6)\text{Cl}$
Reiset's second base . . .	PtNH_3	$(\text{PtNH}_3)\text{O}$	$(\text{PtNH}_3)\text{Cl}$
Gros's base	PtClN_2H_6	$(\text{PtClN}_2\text{H}_6)\text{O}$	$(\text{PtClN}_2\text{H}_6)\text{Cl}$
		(not isolated)	

But little can be at present made out respecting the true constitution of these very interesting compounds.

BICHLORIDE, OR PERCHLORIDE OF PLATINUM, PtCl_2 .

§ 275. *Preparation*.—This salt, commonly called chloride of platinum, is prepared by dissolving the metal in a mixture of two parts of hydrochloric acid and one part of nitric, evaporating the liquid at a gentle heat to the consistence of a syrup, redissolving in dilute hydrochloric acid, and again evaporating, to expel excess of nitric acid; the syrupy liquid solidifies on cooling; care must be taken that it be not overheated. Platinum-wire should not be employed for this purpose, since it dissolves very slowly; pieces of platinum foil and old crucibles should be dissolved; they must be previously cleaned, however, by boiling successively with concentrated nitric acid, with water, and then with concentrated hydrochloric acid.

It is often necessary, in the laboratory, to prepare the bichloride of platinum from *platinum residues*, which should always be saved for this purpose. These residues may contain a great variety of substances, and the pure platinum must be extracted from them as follows; the residues, filters, &c., are evaporated to dryness in a dish, then transferred to a Hessian crucible, and very strongly ignited with excess of air, by which all organic and volatile matters are expelled; the residue is boiled successively with concentrated hydrochloric acid, with water, and with concentrated nitric acid; lastly, again with water (two or three times), and dissolved in nitro-hydrochloric acid; the solution may be evaporated, as

directed above, and if any doubt still exist as to its purity, the residue may be dissolved in alcohol, the solution filtered, and again evaporated.

Properties.—The bichloride of platinum has a dark red-brown color, and does not crystallize; it is deliquescent, and very soluble in water and alcohol. When heated, it leaves, first, the (proto-) chloride, and then the metal.

When a solution of bichloride of platinum is mixed with concentrated sulphuric acid, it gives a dark yellow precipitate, which is the anhydrous bichloride.

Bichloride of platinum combines with many other chlorides to form double-salts.

This salt is a very useful reagent; it is much employed in the laboratory for the precipitation and estimation of potassium and ammonium; it serves, moreover, to convert the hydrochlorates of the organic bases into double-salts, which leave metallic platinum when ignited, from the weight of which we may calculate the atomic weight of the base under examination; since the equivalent of platinum is very high, a loss which would considerably influence other determinations little affects these, so that the atomic weight, determined by experiment, not unfrequently coincides exactly with that ascertained by calculation.

Bichloride of platinum is sometimes used in medicine.

Bichloride of Platinum and Chloride of Potassium, $KCl.PtCl_2$, also sometimes called *potassio-chloride of platinum*, and *platino-chloride of potassium*.—This compound is obtained as a crystalline precipitate, on mixing solutions of its constituent salts, or on adding hydrochloric acid and bichloride of platinum to a solution of any salt of potassa. If the experiment be made with a dilute solution, so that the salt is deposited only on standing, or if the precipitate be dissolved in boiling water, and the solution allowed to cool, crystals of considerable size may be obtained.

The crystals are yellow octohedra; they are decomposed by heat, leaving a mixture of chloride of potassium and metallic platinum. This double chloride requires 144 parts of cold water for solution, but is more soluble in boiling water; the solution is neutral. It is insoluble in alcohol.

Potassium is generally estimated in this form.

Bichloride of Platinum and Chloride of Sodium, or *Platino-Chloride of Sodium*, $NaCl.PtCl_2$.—This salt is very soluble in water, and moderately so in alcohol; it crystallizes in yellow prisms. It is occasionally employed medicinally.

Bichloride of Platinum and Chloride of Ammonium, *Ammonio chloride of Platinum*, $NH_4Cl.PtCl_2$.—The precipitate produced by solution of bichloride of platinum in solution of chloride of ammonium, or of any salt of ammonia, to which hydrochloric acid has been added, consists of this double salt.

It may be crystallized in yellow octohedra in the same way as the potassium-salt. When heated, it is decomposed, leaving metallic platinum. This salt is nearly insoluble in absolute alcohol, one part dissolves in 26,535 parts of alcohol of 77.5 per cent., and 665 parts of alcohol of 45 per cent.

It will be remembered that it is employed as a source of pure platinum.

In this form, also, nitrogen is generally weighed; and if we compare its equivalent (223.2) with that of nitrogen (14), we shall conceive the accuracy with which this element may be determined.

The double-salts formed by bichloride of platinum with the chlorides of barium, strontium, magnesium, and calcium, are soluble and crystallizable; those formed by other metallic chlorides are for the most part insoluble.

SULPHIDES OF PLATINUM.

Two compounds of platinum and sulphur are known, which correspond to the oxides.

Sulphide or Protosulphide of Platinum, PtS , may be prepared by heating two parts of sulphur with one part of finely-divided platinum, when it forms a

gray, brittle mass. It is also obtained when the (proto-) chloride of platinum is decomposed by hydrosulphuric acid or an alkaline sulphide.

The *Bisulphide of Platinum* is precipitated when sulphuretted hydrogen is passed through a neutral or acid solution of the binoxide. It forms a black precipitate, which loses half its sulphur when heated in close vessels. It is insoluble in hydrochloric and sulphuric acids, but dissolves in concentrated nitric acid, being converted into sulphate of binoxide of platinum. It dissolves to some extent, but not readily, in the alkalies and alkaline sulphides, yielding sulphur-salts, from which the bisulphide is reprecipitated by acids.

§ 276. ALLOYS OF PLATINUM.—Iron is capable of forming, with platinum, alloys which are malleable, and possess considerable lustre.

Copper and platinum form a very brilliant alloy, which is sometimes employed for the specula of telescopes.

Platinum hardens silver in a remarkable manner.

It has already been mentioned, that if platinum be alloyed with a sufficient quantity of silver, it becomes soluble in nitric acid.

Other alloys of platinum with lead, tin, antimony, gold, &c., are known, but possess no practical interest.

METALLURGY OF PLATINUM.

This metal is always found native in alluvial deposits similar to those in which gold occurs; in fact, the latter often accompanies the platinum.

It is usually found in small grains, but sometimes in masses, and is associated with osmium, iridium, palladium, rhodium, ruthenium, gold, silver, iron, copper, and several foreign minerals, such as magnetic oxide of iron, titanio iron, chrome iron, pyrites, &c.

When the ore (obtained by washing the sand) contains any considerable quantity of gold, this metal is extracted by amalgamation (*see* p. 399). The ore is then heated with somewhat dilute *aqua regia*, as long as anything is dissolved by a fresh portion of this acid; since, during this operation, very irritating vapors of osmic acid are evolved, it should be performed under a chimney. The solution will contain nearly all the platinum, whilst the residue contains the greater part of the iridium and osmium, which are not soluble in diluted nitro-hydrochloric acid. The solution is evaporated to a small bulk, and mixed with chloride of ammonium, which precipitates the platinum and a little iridium as double chlorides.

The supernatant liquid, which still contains a little platinum, is precipitated by metallic iron, and the finely-divided metal treated with dilute *aqua regia*, which dissolves only the platinum; the solution is precipitated with chloride of ammonium, this precipitate added to the former, the whole washed, dried, and ignited at a dull red heat; in order to convert into malleable metal the spongy platinum thus obtained, it is powdered in a wooden mortar, mixed into a paste with water, and rubbed through a sieve; a wooden mortar is employed, because the use of metal would render some parts of the platinum too compact.

The paste of platinum is introduced into a cylinder of brass, closed by a steel plate, and compressed first with a wooden, and afterwards with a metallic piston; the water is thus squeezed out, and some cohesion given to the metal; it is now submitted to the action of a powerful press, then heated to whiteness, and beaten into malleable platinum upon an anvil; it may then be worked into wire or plate.

Platinum is chiefly used for vessels serving the purposes of the chemist; it is largely employed for the stills in which oil of vitriol is concentrated.

Platinum is also used in porcelain-painting, for that species of ware termed *china-blanc*. In Russia, this metal circulates in the form of coin. It is also used for the touchholes of fowling pieces, on account of its resistance to the action of corrosive agents.

PALLADIUM.

Sym. Pd. Eq. 53.3. Sp. Gr. 11.5.

§ 277. *Preparation.*—This metal occurs in small quantity, associated with native gold and platinum.

It is usually prepared from the mother-liquor remaining after the precipitation of platinum, from its solution in *aqua regia*, by means of chloride of ammonium. It will be remembered that this mother-liquor was decomposed by metallic iron, when a black deposit is formed containing platinum, palladium, rhodium, iridium, gold, lead, and copper. The copper and lead are extracted by weak nitric acid, the residue dissolved in *aqua regia*, the solution neutralized with carbonate of soda, and a solution of cyanide of mercury added, which precipitates the palladium in the form of cyanide; this latter, when ignited, leaves spongy palladium, which may be converted into the malleable metal, in the same manner as platinum.

Properties.—Palladium is one of the hardest metals. Its color is intermediate between that of platinum and silver; it is malleable, ductile, and capable of being welded like platinum. Palladium is very infusible; it may be liquefied in the flame of the oxyhydrogen blowpipe, where it throws off sparks like platinum.

This metal is unalterable in air at the ordinary temperature; when heated in air, it becomes blue, from superficial oxidation, but regains its natural color as the temperature rises, the oxide being decomposed.

Palladium is not capable of decomposing water under any circumstances; concentrated nitric, sulphuric, and hydrochloric acids dissolve it to some extent, but it is much more readily dissolved by *aqua regia*. It combines directly with chlorine, sulphur, carbon, and phosphorus, among the non-metallic elements, and with most of the metals.

Fused potassa attacks palladium, if air be present; a mixture of potassa and nitre very readily corrodes it. It is also attacked by fused bisulphate of potassa.

Uses.—Palladium is sometimes employed instead of silver for the graduated scales of philosophical instruments, since it is not tarnished by sulphuretted hydrogen.

This metal, moreover, is used in the construction of accurate balances and chronometers.

An alloy of palladium, with one-tenth of silver, is employed by dentists.

Palladium forms two oxides corresponding to those of platinum.

OXIDE, OR PROTOXIDE OF PALLADIUM, PdO.

The anhydrous (prot-) oxide is obtained by gently heating the nitrate of palladium; it forms a dark gray metallic-looking powder, which is easily reduced by heat. It dissolves in acids, forming salts, but is not acted on by alkalies.

The *hydrate* is precipitated by adding an alkaline carbonate to nitrate of palladium; it has a brown color, and is soluble both in acids and alkalies.

The salts of oxide of palladium have a red-brown color.

Nitrate of Oxide of Palladium is obtained by dissolving the metal in nitric acid; the solution does not deposit crystals when evaporated, but if ammonia be added, crystals of a double nitrate may be obtained.

Binaxide of Palladium (PdO₂) has not been obtained in a pure state; when the bichloride is decomposed by an alkali or an alkaline carbonate, a brown precipitate is formed, which always contains alkali; this precipitate dissolves in most acids.

(PROTO-) CHLORIDE OF PALLADIUM, PdCl.

This compound is produced when the metal is dissolved in as little nitrohydrochloric acid as possible; it forms a red solution from which crystals of the same color may be obtained by evaporation; it is completely decomposed by heat, yielding first an oxychloride, and afterwards the metal. Chloride of palladium is sometimes used in analysis for separating iodine from chlorine and bromine. This chloride forms double-salts with the chlorides of the alkali-metals.

The *double chloride of palladium and potassium*, PdCl.KCl, and that of *palladium and ammonium*, PdCl.NH₄Cl, are slightly soluble in water, and insoluble in alcohol; they may be obtained in fine crystals.

The corresponding sodium salt, PdCl.NaCl, is deliquescent, and soluble in water.¹

BICHLORIDE OF PALLADIUM, PdCl₂.

The bichloride is formed when the preceding compound is heated with an excess of *aqua regia*, and may be obtained as a brown crystalline mass by evaporation *in vacuo*. It is very unstable, being decomposed when heated, even in a state of solution, into chloride of palladium and chlorine.

When solution of bichloride of palladium is mixed with chloride of potassium, or chloride of ammonium, a red precipitate of a *double chloride* is produced.

A compound of *palladium with carbon* is formed when this metal is heated in the flame of a spirit-lamp.

REACTIONS OF PALLADIUM.—(Prot.) *oxide*.—*Potassa*, *soda*, and *their carbonates*; brownish precipitate, soluble in excess; and reprecipitated from solution in the carbonates by boiling.

Ammonia and *its carbonate*; no precipitate except in the chloride, which gives a flesh-colored precipitate (ammonio-chloride of palladium) soluble in large excess, on standing.

Hydrosulphuric acid and *sulphide of ammonium*; black sulphide of palladium.

Sulphate of iron and (proto-) *chloride of tin*; in concentrated solutions; a black precipitate of reduced palladium, and, in the case of tin, a green supernatant liquid.

Iodide of potassium; black precipitate of iodide of palladium.

Cyanide of mercury; yellowish-white precipitate of cyanide of palladium; produced after a time in acid solutions.

(*Binaxide*).—*Chlorides of potassium and ammonium*; brownish-red precipitate of a double salt, sparingly soluble in water and alcohol.

Solution of the bichloride of palladium evolves chlorine when heated, and is converted into the (proto-) chloride.

RHODIUM.

Sym. Rh. Eq. 52.2. Sp. Gr. 10.6.

§ 278. *Preparation*.—Rhodium is also found in the ores of platinum. It is extracted from them by dissolving the ore in *aqua regia*, precipitating the platinum by chloride of ammonium, neutralizing the solution with carbonate of soda, adding cyanide of mercury to separate the palladium, and evaporating the

¹ A series of ammonia-compounds, similar to those of platinum, have been obtained from the chloride of palladium.

filtered liquid to dryness with excess of hydrochloric acid; the residue is treated with alcohol, which leaves the double chloride of rhodium and sodium undissolved, as a red-brown powder. This salt is heated in a bulb-tube through which a stream of pure hydrogen is passed; the rhodium is thus reduced to the metallic state, and the chloride of sodium may be washed away by water.

Properties.—Rhodium is a grayish-white ductile metal; it is exceedingly hard, and one of the most infusible of the metals; the oxyhydrogen blowpipe-flame only softens it.

This metal is unaltered in air at the ordinary temperature, but, at a red heat, is easily oxidized.

Pure rhodium is not attacked by acids, it even resists the action of *aqua regia*, which dissolves it, however, when alloyed with other metals.

A mixture of potassa and nitre converts rhodium into sesquioxide.

Rhodium is employed, on account of its hardness, for making the nibs of gold pens.

When heated with bisulphate of potassa, the double sulphate of rhodium and potassa is formed.

Two oxides of rhodium are known.

The *Oxide*, RhO , is produced when the finely divided metal is heated in air, but it then becomes partially converted into sesquioxide.

The *Sesquioxide of rhodium*, Rh_2O_3 , is formed when *aqua regia* acts upon alloys of rhodium with other metals.

It may be prepared by fusing finely divided rhodium with a mixture of potassa and nitre, and washing the mass, first with water, then with a dilute acid.

It is thus obtained as a black powder, which is not decomposed by heat.

Hydrated sesquioxide of rhodium is obtained as a yellowish-brown gelatinous precipitate, when a solution of the sesquichloride is boiled with potassa.

Sesquioxide of rhodium combines with acids, forming salts which are red in concentrated, and pink in diluted solutions.

Several intermediate oxides of rhodium also exist.

It is also capable of playing the part of a weak acid, dissolving in alkalies, and forming salts termed *rhodiates*.

CHLORIDES OF RHODIUM.

(*Proto*-) *chloride of rhodium*, RhCl , is obtained by heating rhodium in air, and treating the product with hydrochloric acid, when the sesquioxide which is present is dissolved in the form of sesquichloride, and the (*proto*-) chloride is left as an insoluble reddish powder.

Sesquichloride of rhodium, Rh_2Cl_3 , has a brownish-black color, and does not crystallize. It resists a pretty high temperature without decomposition, and dissolves in water to form a red solution.

Sesquichloride of rhodium forms crystallizable double-salts with the chlorides of the alkali-metals; these compounds are best prepared by heating, in a current of chlorine, a mixture of finely-divided rhodium with an alkaline chloride.

The name of rhodium is derived from the red color of its compounds (*ρῶδον*, a rose).

REACTIONS OF RHODIUM—(*Sesquioxide*).—*Potassa, soda, and their carbonates*; yellowish hydrate, by the former, on boiling, by the latter in the cold, after some time.

Ammonia and its carbonate; yellowish precipitate.

Hydrosulphuric acid and sulphide of ammonium (the former after some time); brown precipitate.

(*Proto*-) *chloride of tin*; dark-red brown color.

Iodide of potassium; similar reaction.

Chlorides of potassium and ammonium; pink precipitates.

Compounds of rhodium may easily be reduced to the metallic state by heating in an atmosphere of hydrogen; the reduced rhodium may be distinguished by its insolubility in *aqua regia*, and its solubility in fused bisulphate of potassa, to which it imparts a pink color.

 IRIDIUM.

Sym. Ir. Eq. 99. Sp. Gr. 16.

§ 279. This metal, which has received the above name in consequence of the various colors of its compounds, occurs in native platinum, generally in combination with osmium, and its extraction will be described in the history of that metal. An alloy of iridium and platinum is also found in nature, crystallized in octohedra, the specific gravity of which is 22.3.

Iridium is obtained, by calcining the ammonio-chloride, in a spongy state, but it may be rendered more compact by pressure. It has a gray color, and its spec. grav. is about 16; but it is generally believed to be even heavier than platinum, from the high specific gravity of the alloy mentioned above.

Iridium is neither malleable nor ductile; it has not yet been fused, and is oxidized if heated and allowed to cool in air. Like rhodium, it is not attacked by acids, unless it be alloyed with platinum, or some other metal, when *aqua regia* dissolves it. It is oxidized by a mixture of potassa and nitre, and is capable of direct combination with chlorine. It is also attacked by bisulphate of potassa at a high temperature.

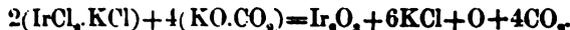
Finely divided iridium (*iridium-black*) possesses properties similar to those of platinum-black.

Iridium forms four oxides; viz: oxide, IrO ; sesquioxide, Ir_2O_3 ; binoxide, IrO_2 ; teroxide, IrO_3 .

The oxide is prepared by decomposing the double chloride of iridium and potassium with an alkaline carbonate, when it is obtained as a greenish-gray precipitate, which dissolves in acids.

This oxide is not decomposed by heat, but may be easily reduced by hydrogen. It is gradually oxidized when exposed to air.

Sesquioxide of Iridium, Ir_2O_3 , is formed when the metal is oxidized by nitre, or by caustic alkalis. It may be prepared by heating the double chloride of iridium and potassium ($\text{IrCl}_2, \text{KCl}$) with carbonate of potassa, in an atmosphere of carbonic acid, and washing the residue with slightly acidulated water:—



The sesquioxide is a black powder, which is reduced to the (prot-) oxide when heated; it is insoluble in acids, but combines with alkalis to form brown, unstable compounds, which are little known.

The most important oxide of iridium is the binoxide, IrO_2 , which is produced when solutions of the lower oxides are boiled in contact with air, or with nitric acid.

When solution of the sesquichloride is heated with potassa in contact with air, no precipitate is formed at first, but oxygen is gradually absorbed; the solution becomes blue, and deposits blue hydrated binoxide of iridium, $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$.

This oxide resembles the binoxide of platinum in its chemical relations; its solutions have a deep red-brown color.

Teroxide of Iridium, IrO_3 , is obtained as a greenish precipitate when terchloride of iridium is decomposed by an alkali.

CHLORIDES OF IRIIDIUM.

The chlorides of iridium correspond to the oxides.

The (*Proto*-) *chloride* is produced when chlorine is passed over finely divided iridium at a red heat; it is formed more readily, if the iridium be mixed with chloride of potassium. It has a dark-green color, and is insoluble in water. The double chlorides which it forms with the chlorides of potassium and ammonium are soluble and crystallizable.

Sesquichloride of Iridium, Ir_2Cl_6 , is formed by dissolving the sesquioxide in hydrochloric acid; it has a very dark color, is deliquescent, and uncrystallizable. It combines with the alkaline chlorides, forming soluble double-salts, which are decomposed by ebullition into soluble salts of the (*proto*-) chloride, and insoluble salts of the bichloride (which are precipitated).

The *Bichloride* (IrCl_4) is the product of the action of nitro-hydrochloric acid upon iridium (alloyed with other metals), or one of its oxides; it is soluble in water, and forms a yellowish-red solution.

This chloride also combines with the chlorides of the alkali-metals.

The *double-salt of bichloride of iridium and chloride of potassium* is soluble in water, and forms a red solution, from which very dark red octohedra may be obtained, having the composition $\text{IrCl}_4 \cdot \text{KCl} \cdot \text{HO}$.

The corresponding compound of ammonium is obtained as a very dark brown precipitate when chloride of ammonium is added to solution of bichloride of iridium; it may be dissolved in boiling water, and crystallized in octohedra. The red color of the ammonio-chloride of platinum is often due to the presence of this salt, which is not materially detrimental to an analysis, since the equivalent of iridium is nearly the same as that of platinum.

The precipitate of ammonio-chloride of iridium dissolves in solution of sulphurous acid, being converted into the double-salt of the (*proto*-) chloride.

Tetrachloride of Iridium, IrCl_4 , is produced when an oxide of iridium is dissolved, at a gentle heat, in very concentrated *aqua regia*.

It is a very dark brown, deliquescent substance, soluble in water, and capable of forming double-salts with the alkaline chlorides.

The *compounds of iridium with sulphur* correspond to the oxides and chlorides. A *carbide of iridium* also exists.

REACTIONS OF IRIIDIUM.—(*Binoxide*).—The *alkalies*, when added in excess to solutions of iridium, produce a greenish color, becoming blue on exposure to air.

The *carbonates of soda* and of *ammonia*, and the *alkaline bicarbonates*; similar reaction.

Carbonate of potassa; a brownish-red precipitate, redissolved spontaneously after some time; the color of the liquid alters as above, upon exposure to air.

Hydrosulphuric acid, and *sulphide of ammonium*; brown precipitate, soluble in sulphide of ammonium.

(*Proto*-) *sulphate of iron* discolors the solution; after some time, a greenish precipitate.

(*Proto*-) *chloride of tin*; a light brownish precipitate.

Chlorides of potassium and ammonium; dark brown precipitates.

OSMIUM.

Sym. Os. Eq. 99.6. Sp. Gr. 10.

§ 280. This metal is prepared from the alloy of iridium and osmium (*osmiridium*), which is found in company with native platinum.

Preparation.—The alloy is mixed with three parts of nitre, and strongly heated for about an hour. The fused mass (containing osmic acid, OsO_4 , and teroxide of iridium) is heated in a retort with a large excess of nitric acid; a considerable quantity of osmic acid distils over, and condenses in white crystals in the receiver. When no more osmic acid passes off, which may be known by the odor, the contents of the retort are mixed with water, the oxides of iridium and osmium collected on a filter, and dissolved in *aqua regia*. The solution is then treated with chloride of ammonium, which precipitates the two metals as double chlorides; these are suspended in water and subjected to a current of sulphurous acid, which reduces the bichloride of iridium to the state of soluble (proto-) chloride, whilst the double chloride of osmium and ammonium is left, and may be reduced by a heating in a current of hydrogen.

The solution containing the double chloride of iridium and ammonium yields crystals on evaporation, and by igniting these, metallic iridium is obtained.

Properties.—Osmium is a grayish, brittle metal, of spec. grav. about 10. When precipitated from its solutions, it has often a bluish color. It cannot be fused, nor volatilized, if air be excluded.

Osmium, in a finely divided state, absorbs oxygen from the air, and is converted into osmic acid; it takes fire in oxygen, even at $212^\circ \text{F. (}100^\circ \text{C.)}$.

When heated on platinum foil in the flame of a spirit-lamp, it is converted into osmic acid, which is volatile, and has a characteristic odor, whereby we are enabled to recognize small quantities of osmium.

Osmium dissolves in nitric acid, being converted into osmic acid.

The alkaline hydrates and nitrates, attack osmium, osmiates being produced.

Five compounds of osmium with oxygen are known, viz: OsO , Os_2O_3 , OsO_2 , OsO_3 , OsO_4 .

Oxide of Osmium (OsO), is obtained as a dark green precipitate when a solution of the double chloride of osmium and potassium is decomposed by potassa.

It is easily reduced by hydrogen, and dissolves in acids, forming green solutions.

Sesquioxide of Osmium (Os_2O_3), is only known in combination with ammonia, and may be obtained by gently heating osmic acid with that reagent; the compound has a dark brown color, and, when boiled with solution of potassa, and subsequently washed, is very explosive. It dissolves in acids, yielding yellow compounds which do not crystallize.

Binoxide of Osmium (OsO_2).—In order to obtain this oxide, a current of chlorine is passed over a mixture of osmium with chloride of potassium, when a compound of bichloride of osmium with chloride of potassium is obtained, which yields the binoxide when heated with carbonate of potassa.

Binoxide of osmium is black; it dissolves in acids, when freshly prepared, forming salts which are little known.

Osmious Acid (OsO_3) is only known in combination; when an attempt is made to isolate it, it is decomposed into osmic acid and binoxide of osmium:—



Osmite of potassa is obtained by decomposing a solution of the osmiate with reducing agents (alcohol or nitrite of potassa). It forms rose-colored crystals, soluble in water, but insoluble in alcohol; its aqueous solution absorbs oxygen from the air, and yields osmiate of potassa.

Osmite of acida is prepared in the same manner, and is more soluble than the osmite of potassa.

OSMIC ACID, OsO_4 .—This acid may be prepared by heating osmium with nitric acid, in a retort, when the osmic acid condenses in the receiver in colorless prismatic crystals, which fuse and volatilize below the boiling point of water, yielding a vapor of a very peculiar, irritating odor, which is dangerous to the operator. Osmic acid should not be handled, for it destroys the skin. It is

very soluble in water, and its solution evolves vapor of osmic acid at the ordinary temperature. Its acid properties are feeble, it neither reddens litmus nor decomposes the carbonates; its salts are unstable.

OSMIUM AND CHLORINE.—When osmium is heated in a current of chlorine, a *chloride* and a *bichloride* are obtained; the former, being less volatile, condenses near to the osmium, whilst the latter is carried to a greater distance.

The (*proto*-) *chloride* has a green color, and is soluble in water, but the solution speedily decomposes, with precipitation of metallic osmium, hydrochloric and osmic acids being produced.

The *bichloride* has an orange-yellow color, is crystalline, very fusible, and deliquescent.

The name of *osmium* has been derived from *οσμή*, *odor*, in consequence of the powerful odor of osmic acid.

REACTIONS OF OSMIUM (Binoxide).—*The alkalis and their carbonates*; after some time or on boiling, a black precipitate.

Hydrosulphuric acid and sulphide of ammonium; brownish-yellow precipitate.

Subnitrate of mercury; yellowish-white precipitate.

Chloride of tin; brownish precipitate.

All compounds of osmium, when boiled with excess of *nitric acid*, evolve the peculiar odor of osmic acid.

RUTHENIUM.

Sym. Ru. Eq. 52.2. Sp. Gr. 8.6.

§ 281. Ruthenium exists in native platinum, alloyed with osmium and iridium.

Preparation.—In order to extract it, the alloy is powdered, mixed with chloride of sodium, and heated to redness in a current of moist chlorine; the mass is extracted with water, and a few drops of ammonia added to the solution, which is then gently heated; a red-brown precipitate is thus obtained, which is a mixture of the oxides of ruthenium and osmium. This precipitate is boiled with concentrated nitric acid, to dryness, when all the osmium is volatilized in the form of osmic acid; the residue is fused in a silver crucible with a mixture of potassa and nitre, and the fused mass digested in a closed flask with cold water free from air; after several hours, the supernatant liquid is decanted, and neutralized with nitric acid, when a black precipitate of sesquioxide of ruthenium is obtained; this precipitate may be washed and heated in a current of hydrogen, to obtain the metal.

Properties.—Ruthenium much resembles iridium; it is brittle, infusible, and scarcely affected by *aqua regia*. Its spec. grav. is said to be only 8.6. Ruthenium is oxidized when heated to redness in air; it forms four oxides.

The *Oxide* (RuO) obtained by heating the chloride with carbonate of soda in a current of carbonic acid, and washing the residue with water, is a dark gray powder with metallic lustre; it is insoluble in acids, and is reduced by hydrogen at the ordinary temperature.

The *Sesquioxide* (Ru₂O₃) is of a dark brown color; it is insoluble in water and alkalis, but dissolves in acids, giving yellow solutions. These produce, with sulphuretted hydrogen, a brown precipitate of sesquisulphide of ruthenium, the supernatant liquid having a blue color.

Binoxide of Ruthenium (RuO₂) is obtained by boiling the sesquisulphide with nitric acid, and decomposing the sulphate of binoxide thus obtained with

an alkali. By calcining the precipitated hydrate, the binoxide is obtained as a greenish-blue powder of metallic appearance.

Ruthenic Acid (RuO_3) is only known in combination with bases; *ruthenate of potassa* is obtained when either of the oxides of ruthenium is heated with nitrate of potassa; it is soluble in water, yielding a yellow solution, from which the acid may be momentarily isolated by adding a stronger acid, but is soon decomposed into binoxide of ruthenium and oxygen.

Chloride of Ruthenium, RuCl_3 , obtained by heating the metal in a current of chlorine, is black, crystalline, insoluble in water and acids.

Sequoichloride of Ruthenium, Ru_2Cl_7 , is formed by dissolving the hydrated sesquioxide in hydrochloric acid, and evaporating to dryness; it has a bluish-green color, and is soluble in water; the aqueous solution yields, with the chlorides of potassium and ammonium, dark brown crystalline precipitates, which are double chlorides.

The *bichloride*, RuCl_4 , is only known in combination with chloride of potassium.

REACTION OF RUTHENIUM (Sesquioxide).—The *alkalies* and their *carbonates*; brown precipitates, soluble in excess.

Hydrosulphuric acid and *sulphide of ammonium*; dark brown precipitate.

Chlorides of potassium and ammonium; dark brown crystalline precipitates.

Cyanide of mercury; blue precipitate, and blue solution.

Nitrate of silver; black precipitate, which becomes lighter on standing, the supernatant liquor acquiring a rose color.

We have now concluded the description of the group of metals found in the ores of platinum, viz. platinum, palladium, rhodium, iridium, osmium, and ruthenium, and it cannot fail to have been observed that a remarkable similarity exists between these metals in their infusibility, and in the disposition of their chlorides to form double-salts with the chlorides of the alkali-metals.

Moreover, a striking coincidence is observed in their equivalents, by which we are enabled to subdivide them into two classes, the first comprising

Platinum	Eq. 98.7
Iridium	“ 99.0
and Osmium	“ 99.6

Whilst the second includes

Rhodium	Eq. 52.2
Palladium	“ 53.3
and Ruthenium	“ 52.2

The differences, it will be perceived, are in all these cases so slight, that probably, were errors of analysis left out of the question, they would actually disappear.¹

ANALYSIS OF THE ORES OF PLATINUM.

§ 282. The complete analysis of the ores of platinum is an operation of such a complicated character, that it would be impossible to describe it here with all the details necessary for its successful execution. We shall therefore content ourselves with giving a general outline of the method adopted, which although of little practical utility, possesses great interest in the eyes of the scientific

¹ This remarkable circumstance would suggest a connection between these metals similar to that pointed out at p. 182, between other analogous elements.

chemist, as one of the best examples of elaborate analysis with which we are acquainted.

The ores of platinum generally contain, besides that metal,

Iron,		Rhodium,
Iridium,		Palladium,
Copper,		Osmium.

It is our intention merely to point out the methods of separating and estimating the rarer metals in this list.

About 30 or 40 grains of the ore are dissolved in *aqua regia*, in a small retort, to which a carefully-cooled receiver is attached. The distillation is continued until the liquid becomes syrupy, and solidifies on cooling. The saline mass is dissolved in the smallest possible quantity of water, and the solution carefully decanted into another vessel. The distilled acid is poured back on to the undissolved residue, and the distillation carried on to the same point as before.

The distillate, which contains the osmium, is diluted with water, and nearly neutralized with ammonia. It is poured into a flask, diluted so as nearly to fill it, and thoroughly saturated with sulphuretted hydrogen; after which the flask is closed with a cork, and set aside for a day or two, till the precipitate has completely separated, leaving the solution clear. The clear liquid is drawn off with a siphon, the sulphide of osmium collected upon a weighed filter, washed, dried, and weighed.

The solution in the retort, and that previously poured out, are mixed together, and filtered off from the residue, which contains a little osmide of iridium, sand, &c., which should be weighed.

The filtered solution is mixed with twice its volume of alcohol of sp.gr. 0.833, and a strong solution of chloride of potassium added, as long as it produces any precipitate, which consists of the potassio-chlorides of platinum and iridium, together with small quantities of the corresponding compounds of rhodium and palladium. The precipitate is collected upon a filter, and washed with alcohol of 60 per cent., mixed with a small quantity of a strong solution of chloride of potassium, until the washings are no longer precipitated by sulphuretted hydrogen.

The precipitate is then dried, mixed with its own weight of carbonate of soda, and heated in a porcelain crucible till the mixture has become black throughout, when the platinum has been reduced to the metallic state.

The mass is washed with water, and when the greater part of the saline matter had been thus removed, the residue is treated with dilute hydrochloric acid, to dissolve the remainder of the alkali, collected on a filter, washed, dried, ignited, and weighed. Its weight represents that of the metallic platinum, together with the sesquioxides of iridium and rhodium. This residue is now fused with five or six parts of bisulphate of potassa, in a platinum crucible. The mass is treated with water, the residue (platinum and sesquioxide of iridium) ignited and weighed.

The solution, containing the rhodium, is mixed with an excess of carbonate of soda, evaporated to dryness, and the residue ignited in a platinum crucible.

The ignited mass is treated with water, when sesquioxide of rhodium remains undissolved; it is collected on a filter, washed, ignited with the filter, and reduced by hydrogen.

The mixture of platinum and sesquioxide of iridium is digested with very dilute *aqua regia*, to remove the platinum. The mixture is allowed to subside, the clear liquid decanted, strong *aqua regia*, mixed with some chloride of sodium, poured over the residue, and the whole evaporated to dryness (the chloride of sodium is added to convert the bichloride of platinum into a double chloride,

and thus to prevent the formation of any (proto-) chloride). The mass is washed, in a filter, with a dilute solution of chloride of sodium, afterwards with dilute chloride of ammonium, dried, and ignited. The iridium is reduced by hydrogen, and weighed. The small quantity of iridium contained in the solution is recovered by adding an excess of carbonate of soda, evaporating and igniting. The residue is washed with water, the platinum removed by *aqua regia*, the residual sesquioxide of iridium washed, dried, reduced by hydrogen, and weighed; its weight is then added to that of the iridium previously obtained.

The amount of the platinum is obtained by difference.

The alcoholic liquid filtered from the double chlorides of platinum, iridium, and rhodium, is poured into a flask, perfectly saturated with sulphuretted hydrogen, the flask closed, and allowed to stand for twelve hours in a warm place. The solution is then filtered, and the alcohol evaporated, any additional precipitate being added to the former one.

The precipitate contains chiefly the sulphides of palladium, iridium, and rhodium; a little iridium and rhodium also remaining in the filtrate.

The sulphides are roasted in a platinum crucible as long as any sulphurous acid is evolved; the residue is treated with concentrated hydrochloric acid, which dissolves a basic sulphate of binoxide of palladium (together with a basic sulphate of copper), leaving the sesquioxide of rhodium and iridium, together with a little platinum.

The hydrochloric solution is mixed with chloride of potassium and a little nitric acid, and evaporated to dryness. The residue is dissolved in boiling water, and the palladium precipitated as cyanide, by solution of cyanide of mercury; the cyanide of palladium, when ignited, leaves the metal.

The residue left by hydrochloric acid is fused with bisulphate of potassa, the mass washed with water, treated with *aqua regia* to remove a little platinum, and the oxide of iridium which is left may be reduced and weighed.

The rhodium in the solution of bisulphate of potassa may be determined according to the directions given above.

The original filtrate from the precipitate produced by sulphuretted hydrogen is heated with nitric acid to peroxidize the iron, which is then precipitated by ammonia, washed, dried, ignited, and weighed. Since it contains a little iridium and rhodium, it must be reduced by hydrogen, and dissolved in hydrochloric acid, when those two metals are left; they are converted into sesquioxides by ignition in the open air, and weighed.

The filtrate from the sesquioxide of iron, which still contains iridium and rhodium, is mixed with excess of carbonate of soda, evaporated to dryness, and the residue heated to dull redness; it is afterwards treated with water, which leaves the sesquioxides of iridium and rhodium undissolved. These may be mixed with the sesquioxides obtained above, and separated, as usual, by fusion with bisulphate of potassa.

TIN.

Sym. Sn. Eq. 58. Sp. Gr. 7.285.

§ 283. This metal and its compounds deserve a considerable share of our attention, since they are applied to a great many useful purposes. Tin not met with in commerce in a state of purity; commercial tin generally contains traces of lead, iron, copper, arsenic, and, sometimes, antimony, zinc, bismuth, molybdenum, tungsten, and manganese. In order to obtain perfectly pure tin,

the ordinary metal is granulated, and dissolved in hydrochloric acid, and the solution concentrated by evaporation. It is allowed to cool in a beaker, and carefully covered with a layer of water; a plate of tin is then introduced, so as to traverse the two layers of liquid, when a feeble galvanic current will be excited, and the pure tin will be deposited in fine crystals.

Properties.—Tin is a white metal, with a very faint tinge of yellow. It is one of the softest and least elastic metals. The malleability of tin is very considerable, but, with the exception of lead, it is the least tenacious of common metals, for a wire of one-tenth of an inch in diameter will support only forty-seven pounds. Tin has a great tendency to crystallize, and the ordinary forms of this metal have a remarkably crystalline texture, as may be shown by rubbing the surface with warm diluted nitro-hydrochloric acid, when it assumes a peculiar diversified appearance, which is termed the *moiré métallique*, and is due to the unequal reflection of light by the facets of the crystals. When a bar of tin is bent, a peculiar crackling sound is heard, caused by the friction of the crystals upon each other.

The fusing point of tin is $442^{\circ} 4$ F. (228° C.). It is very slightly volatile, even at the highest temperatures. When fused tin is allowed to cool gradually, it crystallizes in octohedral prisms. If, when in the fused state, it be poured into a warm iron mortar, and stirred continually till it cools, it may be reduced to powder.

Tin is not altered by exposure to air at the ordinary temperature; when fused in air, it becomes covered with a gray film, containing both oxide and binoxide of tin, and, at a white heat, it burns in air, being entirely converted into the binoxide. It is also capable of decomposing steam at a red heat, binoxide of tin being produced, and hydrogen evolved.

Very strong nitric acid does not act upon tin, but when a little water is added, the metal is very rapidly oxidized (with evolution of binoxide of nitrogen), and converted into metastannic acid, Sn_2O_3 , which is insoluble in water and in nitric acid, so that no tin is found in solution.

When tin is treated with moderately strong nitric acid, it is oxidized partly at the expense of the water, the hydrogen of which, in the nascent state, acting upon the excess of nitric acid, or upon one of the inferior oxides of nitrogen, gives rise to the production of ammonia, and hence nitrate of ammonia is always found in the nitric solution of alloys containing tin.

Tin dissolves slowly in cold or dilute hydrochloric acid, but much more rapidly in the hot concentrated acid, hydrogen being evolved, and (proto-) chloride of tin formed. It has been found that hydrochloric acid holding a quantity of chloride of tin in solution, attacks the metal much less readily than the pure acid, whence arises the difficulty which is experienced in dissolving a quantity of tin entirely in one and the same portion of hydrochloric acid.

Dilute sulphuric acid dissolves tin slowly with the aid of heat, hydrogen being evolved; but the hot concentrated acid rapidly converts this metal into sulphate of the (prot-) oxide, with evolution of sulphurous acid.

The hydrates of potassa and soda act upon tin, at high temperatures, hydrogen being evolved, and a soluble compound of the alkali with metastannic acid produced.

Fused nitre is also capable of oxidizing tin. This metal combines directly, and often very energetically, with chlorine, sulphur, phosphorus, &c. It also forms alloys with many of the metals.

TIN AND OXYGEN.

(Prot-) oxide of Tin	SnO
Binoxide (stannic acid)	SnO ₂
Metastannic acid	Sn ₂ O ₃

Various intermediate oxides of tin exist.

OXIDE OR PROTOXIDE OF TIN, SnO.

§ 284. This oxide presents itself in various forms, according to the manner in which it is obtained.

Preparation.—I. When a solution of (proto-) chloride of tin is precipitated by carbonate of ammonia, and afterwards boiled, the oxide is separated in olive-colored crystalline plates.

II. If an excess of potassa be added to chloride of tin, the precipitate which forms at first is redissolved, and if the solution be evaporated *in vacuo*, black crystals of the oxide are deposited. When this modification is heated, it exhibits a kind of decrepitation, with apparent increase of volume, and is converted into the olive-colored plates.

III. By decomposing chloride of tin with excess of ammonia, boiling the precipitate for some minutes with the supernatant liquid, and afterwards drying it without washing away the chloride of ammonium, a bright red form of the oxide is obtained, which may be converted into the olive-colored variety by merely rubbing in a mortar.

Properties.—When heated in air, oxide of tin burns like tinder, and is converted into the binoxide. It is insoluble in water, and in alkaline solutions, but dissolves readily in acids, forming salts.

The *hydrate* (SnO.HO) is precipitated when chloride of tin is decomposed by an alkali, or its carbonate.¹ It forms a white precipitate, which absorbs oxygen from the air, and dissolves readily in acids and alkalies.

When a solution of this hydrate in an excess of potassa is rapidly boiled, the oxide is decomposed into metallic tin, which separates, and stannic acid, which combines with the alkali:—



The salts of oxide of tin are not very well known.

The *sulphate* (SnO.SO₂) may be prepared by dissolving the recently-precipitated hydrate in hot dilute sulphuric acid, when the new salt is deposited, on cooling, in crystalline plates, which are easily soluble in cold water, forming an acid solution. When their solution is heated, a basic sulphate is deposited. The double-salts which this sulphate forms with alkaline sulphates are crystallizable, and more stable than the sulphate itself.

When the hydrated oxide is dissolved in dilute nitric acid, *nitrate of oxide of tin* is formed, but on evaporation, this salt is decomposed, binoxide of tin being deposited. When the metal is treated with nitric acid of spec. grav. 1.114, a solution of a double nitrate of oxide of tin and oxide of ammonium is obtained, which deposits binoxide of tin when boiled.

¹ According to Schaffner, the precipitate produced by ammonia is a basic salt, and the true formula of the hydrate is 2SnO.HO.

BINOXIDE OF TIN, STANNIC ACID.

SnO₂. Eq. 74.

§ 285. This compound (which occurs in nature as *tin-stone*) may be prepared by decomposing the bichloride of tin with water,¹ or by adding an acid to a soluble stannate.

It is thus obtained as a hydrate, forming a white gelatinous precipitate, which is soluble in an excess of acids and alkalies; when dried *in vacuo*, its composition is represented by SnO₂.HO; when strongly heated, it is converted into a yellow hard mass, said to be metastannic acid, Sn₂O₁₀.

Binoxide of tin is sometimes used for polishing, under the name of *putty-powder*.

The binoxide of tin appears to possess a decidedly acid character, for no definite compound of this substance with an acid has hitherto been obtained, whilst, with bases, it forms a series of salts termed stannates.

STANNATE OF POTASSA (KO.SnO₂.4Aq) is obtained by dissolving stannic acid in potassa, or by fusing metastannic acid with this alkali in a silver crucible; by evaporating the aqueous solution *in vacuo*, the stannate may be obtained in white prismatic crystals, which are very soluble in water, and insoluble in alcohol. The aqueous solution is strongly alkaline, and decomposes after a time into potassa and metastannate of potassa.

Almost all soluble salts, even those of the alkalies, cause a precipitate in solution of stannate of potassa.

STANNATE OF SODA (NaO.SnO₂.4Aq) much resembles the potassa salt; it is more soluble in cold than in hot water, so that its aqueous solution becomes turbid when boiled.

The alkaline stannates are used as mordants in dyeing and calico-printing. Stannate of soda is prepared on a large scale by boiling sheets or scraps of tin, and litharge or sulphate of lead, with solution of caustic soda. The lead compounds yield their oxygen to the tin, and greatly facilitate the oxidation; the lead-powder obtained as secondary product may be reoxidized by exposure to air, and again employed for the oxidation of fresh quantities of tin.

The *Stannate of Oxide of Tin* (SnO.SnO₂), or, as it is sometimes termed, *sesquioxide of tin*, is obtained by the action of hydrated sesquioxide of iron upon chloride of tin:—



It forms a yellowish precipitate, which becomes black when heated in close vessels; it is soluble in ammonia.

Binoxide of tin is used in the manufacture of opaque white glass; it is also employed, in conjunction with small quantities of sesquioxide of chromium, for producing certain red and lilac colors, which are employed for coloring earthenware, and for paper-staining.

METASTANNIC ACID, Sn₂O₁₀.

This acid was for a long time regarded as a modification of stannic acid.

It is obtained as a white powder by the action of nitric acid upon tin.

Metastannic acid thus prepared is crystalline; when dried in air, it has the composition Sn₂O₁₀.10HO, but loses 5 eqs. water at the boiling-point; all the water may be expelled at a higher temperature. It is completely insoluble in water, in nitric acid, and dilute sulphuric acid, but dissolves to some extent in concentrated sulphuric and hydrochloric acids; tartaric acid and bitartrate of potassa are also capable of dissolving metastannic acid to a slight extent.

¹ Daubr e has obtained very hard lustrous crystals of the binoxide by passing the vapor of bichloride of tin, mixed with steam, through a redhot porcelain tube.

Metastannic acid dissolves in potassa, forming a metastannate; when freshly precipitated from its salts by acids, it is soluble in ammonia, but not after boiling in the liquid.

When fused with alkalis, metastannic acid is converted into a stannate.

Metastannate of Potassa ($\text{KO.Sn}_2\text{O}_3, 4\text{Aq}$) may be obtained in the pure state by dissolving some hydrate of potassa in the solution of metastannic acid in potassa, when the metastannate, being insoluble in an excess of potassa, is precipitated.

This salt cannot be crystallized; it is very soluble in water, and has a powerful alkaline reaction. It cannot be rendered anhydrous without undergoing decomposition; when metastannate of potassa is heated to redness, and the mass extracted with water, the potassa alone is dissolved, and metastannic acid remains.

The *Metastannate of Soda* is quite similar.

Metastannate of Oxide of Tin ($\text{SnO.Sn}_2\text{O}_3, 4\text{Aq}$) is obtained as a yellow insoluble substance by the action of chloride of tin upon metastannic acid:—



CHLORIDE OR PROTOCHLORIDE OF TIN, SnCl_2 .

§ 286. This useful salt may be prepared in the anhydrous state by the action of hydrochloric acid gas upon tin at a gentle heat, or by distilling powdered tin with an equal weight of chloride of mercury.

Thus obtained, it is a brilliant gray solid, which volatilizes at a bright red heat; it takes fire in chlorine, and is converted into the bichloride.

Hydrated chloride of tin is obtained by dissolving the metal in hydrochloric acid; the concentrated acid should be diluted with an equal bulk of water; the solution is decanted from the undissolved metal, and evaporated to crystallization.

It crystallizes in transparent needles, having the composition $\text{SnCl}_2, 2\text{Aq}$; these are somewhat deliquescent, and absorb oxygen when exposed to air, yielding a combination of binoxide and bichloride of tin; when heated, the crystals lose their water, and a partial decomposition takes place, some hydrochloric acid being disengaged, but, at a higher temperature, great part of the salt may be distilled unchanged.

The chloride of tin is very soluble in water; a large quantity of water, however, decomposes it, an *oxy-chloride of tin* ($\text{SnCl}_2, \text{SnO}$) being deposited.

Chloride of tin is a very powerful deoxidizing agent, it reduces the metals from the salts of silver, mercury, and gold, and brings oxide of copper, sesquioxide of iron, and many other oxides to a lower state of oxidation; hence this salt is often employed as a reagent; it is also used by dyers, sometimes as a mordant, and sometimes to alter the reducible coloring matters, such as sesquioxide of iron and binoxide of manganese.¹ Chloride of tin is also used as an antichlore (see p. 259).

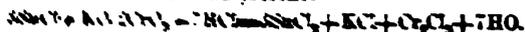
The alkaline chlorides form crystalline double-salts with chloride of tin. It absorbs ammoniacal gas.

BICHLORIDE OR PERCHLORIDE OF TIN.

(*King's Liquor of Liliarius*) SnCl_4 .

Preparation — This compound may be prepared by the direct combination of its constituents. A quantity of tinfil is rolled up, and introduced into a tube

¹ For the expeditious determination of the value of any specimen of chloride of tin, Penny makes use of a solution of the hydrate of potassa of known strength, which is added to the liquid containing the hydrochloric acid, until a portion tested with acetate of lead shows that an excess of chlorine is present. The following equation then gives the data for calculating the amount of chlorine present:—



of hard glass, placed at a very slight inclination, and connected, at the lower end, with an appropriate receiver, and at the other with an apparatus evolving dry chlorine; the tube should be constricted somewhat at the lower end, so as to form a shoulder upon which the tin may rest; it is only necessary to heat the metal gently while the chlorine is passing, when combination ensues, attended with combustion, and the bichloride distils over. The product may be freed from excess of chlorine by agitation with a little granulated tin, and rectification.

A solution of the bichloride may be obtained by dissolving the metal in nitrohydrochloric acid, but a better method consists in boiling granulated tin for a few hours with moderately strong hydrochloric acid, and passing chlorine through the solution (containing the undissolved tin) until it no longer precipitates solution of (proto-) chloride of mercury (corrosive sublimate); the excess of chlorine may then be expelled by a slow evaporation.

Properties.—When pure, bichloride of tin is a colorless liquid, which evolves suffocating white fumes in the air; its spec. grav. 2.28; it boils at 248° F. (120° C.), yielding a vapor of spec. grav. 9.2. It has a powerful affinity for water, combining with it, with a hissing sound, to form a hydrate, which is deposited in crystals of the formula $\text{SnCl}_2 + 5\text{Aq}$, which lose three eqs. water when exposed, *in vacuo*, over sulphuric acid; its aqueous solution is partly decomposed by evaporation, hydrochloric acid being evolved, and stannic acid deposited.¹

Bichloride of tin is capable of absorbing sulphuretted and phosphuretted hydrogen. It combines also with ammonia, and with various organic substances.

This salt forms, with many other chlorides, compounds which may be termed chlorostannates, in which the bichloride of tin plays the part of an acid.

The chlorostannates of chloride of potassium and of chloride of ammonium are anhydrous, and crystallize in octohedra, having the composition, respectively, $\text{KCl} \cdot \text{SnCl}_2$, and $\text{NH}_4\text{Cl} \cdot \text{SnCl}_2$; the corresponding compounds of the chlorides of sodium and of the metals of the alkaline earths crystallize with 5 eqs. water.

Bichloride of tin is used, to a considerable extent, in dyeing.

TIN AND SULPHUR.

Sulphide of tin	SnS
Bisulphide "	SnS_2

SULPHIDE OR PROTOSULPHIDE OF TIN, SnS_2 .

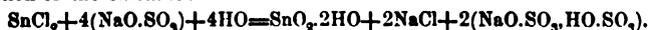
This substance is obtained by heating granulated tin with sulphur, reducing the mass to powder, and fusing it with an additional quantity of sulphur; thus obtained, it is a brilliant, dark, gray, crystalline mass. It is precipitated in a hydrated state when sulphuretted hydrogen is passed through a solution of a proto-salt of tin; it is then black.

Sulphide of tin dissolves in concentrated hydrochloric acid, with disengagement of sulphuretted hydrogen; nitric acid converts it into metastannic acid; it is not soluble in sulphide of ammonium, unless an excess of sulphur be present, which converts the sulphide into bisulphide.

This sulphide is a pretty powerful sulphur-base.

A *sesquisulphide of tin*, Sn_2S_3 (probably a compound of sulphide and bisul-

¹ Löwenthal found that bichloride of tin was decomposed by the alkaline sulphates with precipitation of the binoxide:—



Since a solution of (proto-) chloride of tin is not affected by alkaline sulphates if air be excluded, it is proposed to employ these salts for the detection of bichloride of tin in the chloride. Löwenthal also suggests that this reaction may be turned to account in dyeing.

phide), is obtained when the sulphide is heated to dull redness with an excess of sulphur.

BISULPHIDE OF TIN, SnS_2 .

This compound, when prepared in the dry way, is known by the name of *aurum musivum*, or *Mosaic gold*, which is used for gilding wood and decorating paper; it is commonly termed *bronze-powder*.

In order to prepare it, an amalgam is made of 12 parts of tin and 6 parts of mercury; this is mixed with 7 parts of flowers of sulphur and 6 of sal-ammoniac; the mixture is then heated (in a glass flask placed in a sand-bath) to dull redness, until no more white fumes are disengaged; the bisulphide is left as a yellow crystalline layer at the lower part of the flask; in this process, the sole use of the mercury appears to be to effect the fine division of the metallic tin, thus facilitating its combination with the sulphur; the bisulphide of tin thus formed, however, is amorphous, and only becomes crystalline after a sublimation, which is promoted by the volatilization of the chloride of ammonium; this latter also serves (by rendering a large amount of heat latent) to prevent the temperature in the flask from rising sufficiently high to convert the bisulphide into sulphide.

The product of this operation forms very light golden-yellow hexagonal plates, which are attacked only by nitro-hydrochloric acid.

Similar scales are obtained when a mixture of sulphuretted hydrogen and vapor of bichloride of tin is passed through a tube heated to dull redness.

The hydrated bisulphide is thrown down as a light yellow precipitate, when sulphuretted hydrogen is passed through solution of bichloride of tin; if the latter be not perfectly pure, but contain, as is often the case, a trace of antimony, the precipitate will have a dirty yellow color. This precipitate dissolves with difficulty in concentrated hydrochloric acid, but, being a powerful sulphur-acid, it is readily soluble in the alkaline sulphides, or even in the pure alkalis or their carbonates.

METALLURGY OF TIN.

§ 287. The only ore of tin, properly so called, is the binoxide, or *tin-stone*, which occurs in a crystalline form, often associated with wolfram, sulphide of molybdenum, and arsenical-pyrites. It has usually a brown or red-brown color, and is very hard.

Tin is also found in Cornwall, combined with sulphur, in *tin-pyrites*, which contains also sulphide of copper.

The metal is always extracted from the binoxide, which occurs sometimes associated with other ores in veins (*mine-tin*), and sometimes as an alluvial deposit in the beds of rivers (*stream-tin*).

The ore is pounded in stamping-mills, and submitted to a species of rough levigation, which washes away the earthy matter and all light impurities; it is then roasted, to expel the sulphur and arsenic, and mixed with about one-eighth of its weight of small coal; the mixture is heated in a reverberatory furnace, and the fused metal run into moulds.

Any considerable quantity of copper is removed from the ore, previously to smelting, by exposure to air and subsequent treatment with sulphuric acid.

If the ore contain wolfram (tungstate of iron and manganese), it undergoes, previously to reduction, a purification which consists in fusing it with carbonate of soda, in a reverberatory furnace, when the tungsten is removed in the form of tungstate of soda, which is used by calico-printers.

The pigs of tin thus obtained are sometimes subjected to a refining process (termed *topping*), which consists in gradually remelting them on a gently inclined hearth, and allowing the portion which first fuses to flow into a large basin,

where a mechanical separation of the remaining impurities is effected, either by stirring the melted metal with billets of green wood (when the gases evolved give rise to considerable agitation), or by throwing portions of the metal repeatedly from a ladle raised to a considerable height (*tossing*). The impurities are carefully skimmed off from time to time. The metal remaining on the liquation-hearth, which is much less pure, constitutes the ordinary block-tin; the purer kind is generally heated to a temperature somewhat exceeding 212° , and allowed to fall from a height, when, being brittle, it is divided into small fragments which are known in commerce as grain-tin.

A process for obtaining very pure metal from stream-tin, consists in reducing the ore with charcoal in a small-blast furnace (*see* Iron).

Tin is generally examined as to its purity by fusing it at a gentle heat, and observing its surface at the moment of solidification; the purest tin is whitest, most brilliant, and least crystalline in appearance.

USES OF TIN.—Since this metal is not easily affected by most chemical agents, it serves very advantageously to protect the surface of such as are more easily acted upon, such as copper and iron; moreover, it is employed, in the state of foil, for preserving substances from the action of air, and for silvering looking-glasses; this metal is also an ingredient of many useful alloys.

Tin foil is prepared by beating plates of the best tin with a hammer till they are reduced to a certain thickness, when they are cut up, laid upon each other, and again beaten, the process being repeated till they have attained the required extension.

Tinned iron, or tin-plate, as it is commonly called, consists of a plate of iron covered with a layer of an alloy of that metal with tin, and, externally, with a layer of pure tin; the process for manufacturing tin-plate is as follows: The iron plates are first thoroughly cleansed with hydrochloric and sulphuric acids, then well washed with water, and scoured with sand to remove all trace of rust, which would prevent the tin from adhering; the plates are then immersed in a bath of melted tallow, which dries them thoroughly, and are removed from this into a bath of tin, the surface of which is covered with tallow, to prevent oxidation; after being heated for about an hour and a half in the melted metal, they are taken out, drained, plunged into another bath of melted tin, and brushed to remove the excess of this metal, afterwards again dipped to erase the marks of the brush, and, lastly, immersed in the melted tallow to remove the small quantity of superfluous tin.

This tin-plate is exceedingly durable, but if, by accident, the iron should be exposed in any part, it rusts very rapidly, from galvanic action.¹

In order to give an internal coating of tin to copper vessels for culinary purposes, they are first cleaned very carefully, a quantity of sal-ammoniac strewed over the surface, to protect it from oxidation, the vessel then made sufficiently hot to melt tin, which, either in the pure state, or alloyed with a certain amount of lead, is then rubbed over them.

Tin is the chief ingredient of the alloy known as *Britannia metal*, which contains, moreover, antimony, copper, and a little lead, the proportions varying according to the judgment of the manufacturer.

The better kinds of *pewter* are alloys of tin with small quantities of copper, lead, and sometimes antimony and bismuth.

ASSAY OF TIN ORES.—The assay of ores of tin is attended with considerable difficulty, on account of the affinity which exists between the oxides of tin and silica.

The powdered ore is first freed, as far as possible, from silicious gangue, by

¹ It has been proposed to alloy the tin employed for this purpose with $\frac{1}{8}$ of nickel, which renders the coating more durable and less easily fusible.

roasting it, in an earthen crucible, with a little powdered charcoal (to assist it in the expulsion of the arsenic, &c.), and afterwards roughly levigated in a porcelain dish, to remove the lighter particles. The heavier portion may then be boiled with nitro-hydrochloric acid, to remove the pyrites, &c., water added, the residue collected on a filter, well washed and dried. It is then removed from the filter, and roasted in a wide open crucible, to expel any sulphur which may be left. The ore thus prepared is mixed with 30 or 40 per cent. of a mixture of equal parts of borax and carbonate of soda, and reduced in a crucible lined with charcoal, at the same temperature as that used for an iron assay. The button is afterwards extracted and weighed.

A far more accurate method of analyzing an ore of tin is executed as follows:—

The powdered ore is heated to redness, in order to expel any water; it is then weighed in a small porcelain boat, and introduced into a tube of porcelain, or hard glass, through which a stream of dry hydrogen is passed. The tube is heated to dull redness by a gas-burner or a charcoal fire, when the binoxide of tin is easily reduced. The reduced residue is allowed to cool in the atmosphere of hydrogen, and the tin dissolved in hydrochloric acid, with the aid of a few drops of nitric acid.

The weight of the tin may then be either directly ascertained, by determining it in the solution, or by calculation from the amount of silica left undissolved, which is collected, for that purpose, on a filter, washed, dried, ignited, and weighed. This latter method is obviously applicable only when no other metal but tin is present in the ore.

ANTIMONY.

Sym. Sb. Eq. 129. Sp. Gr. 6.702.

§ 288. This metal is found in commerce in a very impure state; the *regulus of antimony*, as it is termed, contains generally sulphur, arsenic, iron, and lead. Its purification is attended with considerable difficulty.

Wöhler recommends that 1 part of crude antimony be fused with $1\frac{1}{2}$ part of nitre and $\frac{1}{2}$ part of carbonate of soda, for about an hour; the fused mass powdered, and washed with boiling water, which leaves antimoniate of soda undissolved; this may be reduced by fusion with black flux: since the metal thus obtained contains a little potassium, it should be reduced to powder, and washed with water till the washings are no longer alkaline; the pure metal is then fused into a globule.

Lachig fuses 16 parts of powdered antimony, in a Hessian crucible, with one part of native tersulphide of antimony, and two parts of carbonate of soda; the latter decomposes the tersulphide of antimony, producing sulphide of sodium, which combines with the tersulphide of arsenic. The globule of antimony is afterwards fused for two hours with carbonate of soda.¹

A very efficient method of removing the impurities from crude antimony, consists in dissolving the metal in a mixture of equal volumes of concentrated hydrosulphuric acid and water, to which moderately dilute nitric acid (one part of concentrated acid and two parts of water) is added, by small portions at a time; the solution of antimoniate of antimony thus obtained is largely diluted with water, the precipitate is allowed to subside, washed, first, by decantation,

¹ According to Berzelius, this method is successful only when the metal contains iron: in other cases he recommends the addition of two per cent. of sulphide of iron to the original mass.

and afterwards on a filter, and boiled with concentrated hydrochloric acid; the filtered solution is mixed with a very slight excess of ammonia, the precipitate well washed and dried; this precipitate may serve either for the preparation of other compounds of antimony (the tersulphide, *e. g.*) in a pure state, or may be fused with black flux, when it yields the pure metal.

Properties.—Antimony is a very brilliant metal, of rather a blackish-gray color; it is exceedingly brittle, and may be easily powdered. In texture, it is lamellar and highly crystalline, the primitive form of its crystals being the octohedron; it is unaltered by exposure to air at the ordinary temperature.

Antimony fuses at about 800° F. (427° C.), and volatilizes very perceptibly at a somewhat higher temperature; it is not, however, sufficiently volatile to be distilled like zinc. Fused antimony crystallizes on cooling.

Heated in contact with air, the metal becomes covered with a film of crystallized teroxide of antimony, mixed with antimonic acid; if, when strongly heated, the fused globule be allowed to fall upon the ground, it is divided into numerous smaller globules, which burn very brilliantly, giving off white fumes.

At a red heat, antimony decomposes water, being converted into teroxide.

This metal is readily oxidized by nitric acid, being converted into a white compound of teroxide of antimony with antimonic acid, $Sb_2O_3, Sb_2O_5 (= 2SbO_4)$ antimonic acid). A small quantity of antimony is always found in the nitric solution; a little nitrate of ammonia is also produced in this reaction (*see* p. 129).

Hydrochloric acid acts very slowly upon antimony, but *aqua regia* dissolves it with ease.

It does not decompose water in presence of sulphuric acid, but the concentrated acid converts it, with the aid of heat, into sulphate of teroxide of antimony, with evolution of sulphurous acid.

ANTIMONY AND OXYGEN.

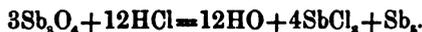
Suboxide	Sb_2O_4
Teroxide	Sb_2O_3
Antimonic acid	SbO_5^1

Some chemists also admit the existence of an oxide of the formula Sb_2O_4 (antimonious acid), but we prefer to consider this as a compound of the teroxide with antimonic acid.

§ 289. SUBOXIDE OF ANTIMONY (Sb_2O_4) constitutes the film which is formed upon the surface of antimony exposed to the action of moist air.

It may be obtained by decomposing a concentrated solution of tartar-emetie (tartrate of antimony and potassa) by a powerful galvanic battery, when the nascent hydrogen of the water reduces the teroxide of antimony to the state of suboxide; it is black, and assumes a metallic lustre when rubbed. When heated, it is decomposed into metal and teroxide.

Hydrochloric acid converts it into terchloride of antimony, with separation of the metal:—



• TEROXIDE OF ANTIMONY, Sb_2O_3 (*Sesquioxide of Antimony, Sb_2O_3*).

Eq. 153.

This oxide is formed when antimony is heated in air. It is also found in nature as *white antimony-ore*.

¹ The equivalent of antimony is sometimes estimated at 64.5, being the half of 129, as we have considered it. Upon that view, the above oxides would be written with twice the number of equivalents of metal; thus teroxide of antimony becomes a sesquioxide, Sb_2O_6 , and antimonic acid is Sb_2O_5 .

The anhydrous teroxide may be prepared in quantity by fusing antimony in a capacious Hessian crucible, over which another crucible (with a hole in the bottom) is inverted; the teroxide will condense in the uppermost crucible in needle-like crystals, which were formerly called *argentine flowers of antimony*.

It is of a pearly-white color, and is capable of crystallizing in two distinct forms, one of which is a regular octohedron, and the other belongs to the prismatic system; in this respect, it resembles arsenious acid, with which it is isomorphous. When heated to redness, teroxide of antimony fuses, and, at a high temperature, sublimes in brilliant needles.

If heated in contact with air, it absorbs oxygen, and is converted into the antimoniate of teroxide of antimony, $\text{SbO}_3, \text{SbO}_5$.

It is easily reduced by hydrogen or charcoal at a high temperature.

Hydrated teroxide of antimony (SbO_3, HO) may be obtained by precipitating a solution of the terchloride in dilute hydrochloric acid, with carbonate of potassa or soda in slight excess, and digesting the precipitate for some time with the supernatant liquid.

The hydrate is readily soluble in acids and alkalies, whence it would appear that the teroxide was capable of playing the part of a base, or of an acid, indifferently. However, on evaporating the alkaline solution, anhydrous teroxide of antimony is deposited. When heated, the hydrate assumes a yellow tint.

When teroxide of antimony is fused with alkalies, in presence of oxygen, the latter is absorbed, and antimoniates are produced.

The soluble neutral salts of teroxide of antimony redden litmus-paper.

Basic nitrate of teroxide of antimony ($2\text{SbO}_3, \text{NO}_3$) is obtained in a crystalline form when teroxide of antimony is dissolved in fuming nitric acid; it is decomposed by water, the teroxide being left undissolved.

SULPHATES OF TEROXIDE OF ANTIMONY.

The salts of teroxide of antimony present an anomaly similar to that observed in the case of uranium. The neutral salts of the teroxide do not contain, as would be expected, three equivalents, but only one equivalent of base, a circumstance, which Péligré explains by assuming the existence of a radical, *antimonyle* SbO_2 (or Sb_2O_3) of which the protoxide would be expressed by $(\text{SbO}_2)\text{O}=\text{SbO}_2$ (or by $(\text{Sb}_2\text{O}_3)\text{O}=\text{Sb}_2\text{O}_3$).

Four sulphates of teroxide of antimony have been examined by this chemist.

The sulphate of the formula $\text{SbO}_3, 4\text{SO}_3$ is obtained in crystalline needles, when oxychloride of antimony is treated with mono-hydrated sulphuric acid.

The salt $\text{SbO}_3, 2\text{SO}_3$ is deposited in small crystals from a solution of the teroxide in Nordhausen sulphuric acid.

When either of these salts is treated with hot water, the (neutral) sulphate, $\text{SbO}_3, \text{SO}_3, 2\text{HO}$, is obtained.

The sulphate of the formula $2\text{SbO}_3, \text{SO}_3$ is obtained from the residue left by the action of oil of vitriol upon metallic antimony, by digesting it with cold water.

§ 290. The highest oxide of antimony, like the binoxide of tin, was formerly considered capable of existing in two distinct modifications, but it has been recently proved that these are two independent acids, differing in their capacity of saturation, and designated, respectively, *antimonic* and *metantimonic* acid. •

ANTIMONIC ACID, $\text{SbO}_5(\text{Sb}_2\text{O}_3)$.

This acid may be obtained by the action of strong nitric acid upon antimony; it is then, however, generally combined with teroxide of antimony; it may be prepared in the pure state by decomposing an antimoniate with dilute nitric acid.

The acid thus prepared is hydrated, having the composition $\text{SbO}_5, 5\text{HO}$; it is

white, slightly soluble in water, and capable of feebly reddening litmus; it is insoluble in dilute mineral acids, but dissolves in potassa or ammonia.

When heated, it assumes a pale yellow color, and is converted into the anhydrous antimonie acid, which, if further heated, loses oxygen, and is converted into the antimoniate of teroxide of antimony ($\text{SbO}_3 \cdot \text{SbO}_3$).

Antimonie acid combines with one equivalent of basic protoxides, forming a class of salts termed *antimoniates*.

ANTIMONIATE OF POTASSA, $\text{KO} \cdot \text{SbO}_3$.

This salt is prepared by gradually adding one part of powdered antimony to four parts of nitre, fused in a Hessian crucible; the fused mass is powdered, washed with warm water, which removes the excess of nitre and the nitrite of potassa, and leaves the anhydrous antimoniate of potassa, which is boiled for an hour or two with water, when it becomes hydrated and dissolves, a little bi-antimoniate of potassa ($\text{KO} \cdot 2\text{SbO}_3$) being left. The clear liquid, when slowly evaporated, leaves a gummy mass, of the composition $\text{KO} \cdot \text{SbO}_3 \cdot 5\text{HO}$.

Antimoniate of potassa has an alkaline reaction.

At 320°F . (160°C .) it loses two equivalents of water, and becomes insoluble; at a higher temperature the whole of the water is expelled, but the original soluble salt is reproduced by continued boiling with water.

Antimoniate of potassa is less soluble in saline solutions than in water, so that many salts precipitate it, as a white gelatinous mass, from its aqueous solution.

A solution of this salt is easily decomposed by acids, hydrated antimonie acid being precipitated. When carbonic acid is passed into its solution, the *bi-antimoniate*, $\text{KO} \cdot 2\text{SbO}_3$, is precipitated.

The *antimoniates of soda* resemble the potassa-salts.

Two *antimoniates of ammonia* are also known; they are insoluble in water.

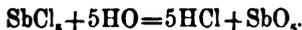
ANTIMONIATE OF TEROXIDE OF ANTIMONY, $\text{SbO}_3 \cdot \text{SbO}_3$.—It has been already remarked that this substance was formerly regarded as an independent acid, represented by the formula SbO_4 , and termed *antimonious acid*.

This compound is always obtained when antimonie acid is heated as long as it evolves oxygen; it may therefore be very readily prepared by oxidizing antimony with nitric acid, and strongly igniting the residue, when the antimoniate remains as a white powder, insoluble in water.

Alkaline solutions decompose it, dissolving the antimonie acid, and leaving teroxide of antimony. If it be boiled with solution of bi-tartrate of potassa, the teroxide is dissolved, and antimonie acid left.

METANTIMONIC ACID, SbO_3 .

This acid is prepared by decomposing the pentachloride of antimony with much water:—



It forms a white precipitate, which only differs from antimonie acid in containing four eqs. water, and in requiring two eqs. of a protoxide to form a neutral salt, so that the general formula of the metantimonates is $2\text{MO} \cdot \text{SbO}_3$; this acid is also capable of producing a class of *acid* salts of the general formula $\text{MO} \cdot \text{SbO}_3$, isomeric with the neutral antimonates.

An antimoniate may be converted into a metantimoniate by fusing with an excess of base; and conversely, the latter into the former, by removing one eq. of base.

METANTIMONIATE OF POTASSA ($2\text{KO} \cdot \text{SbO}_3$) is prepared by fusing antimonie acid with a large excess of potassa in a silver crucible; the mass is dissolved in a little water, and the solution evaporated *in vacuo*, when crystals of the metantimoniate are obtained.

This salt is deliquescent, and very soluble in water, yielding an alkaline solution; it is soluble without decomposition in a liquid containing excess of potassa, but is decomposed by cold water into potassa and bi-metantimoniate of potassa, whence the solution gives, with salts of soda, a white crystalline precipitate of bi-metantimoniate of soda.

BI-METANTIMONATE OF POTASSA (KO.SbO_3) possesses some importance, since it is occasionally used as a test for soda; but, unfortunately, it is so liable to furnish precipitates in solutions containing traces of other metallic oxides (lime, baryta, magnesia, &c.), that little faith is generally placed in its indications.

This salt is prepared by deflagrating 1 part of antimony with 4 parts of nitre, washing the fused mass with warm water, and subsequently boiling with water till as much as possible has been dissolved; the liquid filtered from the insoluble bi-antimoniate is now evaporated in a silver capsule to a syrupy consistence, a few fragments of caustic potassa added (to convert the antimoniate of potassa into metantimoniate), and the evaporation continued till a drop of the liquid crystallizes on a glass plate; on cooling, a crystalline deposit is formed, which consists of a mixture of metantimoniate and bi-metantimoniate of potassa; this is washed rapidly (four or five times) with cold water, to remove the excess of potassa, and to convert all the metantimoniate into bi-metantimoniate, and afterwards agitated for some time with water, when enough of the bi-metantimoniate will be dissolved to enable the filtered liquid to serve to detect very small quantities of soda.¹

The bi-metantimoniate of potassa, prepared as above, is a white crystalline salt, having the composition $\text{KO.SbO}_3.7\text{HO}$; when heated, it loses 2 eqs. of water, and is converted into antimoniate of potassa.

Bi-metantimoniate of Soda has the formula $\text{NaO.SbO}_3.7\text{HO}$; it is very slightly soluble in cold, but more soluble in boiling water.

Metantimoniate of Ammonia is formed when metantimonic acid is dissolved in ammonia; this salt is soluble in water, but if a few drops of alcohol be added to the solution, the *bi-metantimoniate* ($\text{NH}_3\text{O.SbO}_3.6\text{HO}$) is precipitated; this last salt, like the corresponding potassa-compound, is slightly soluble in water.

When kept for some time (even in sealed tubes) it is transformed into antimoniate of ammonia ($\text{NH}_3\text{O.SbO}_3.4\text{HO}$), which is insoluble in water. The same change takes place immediately on heating.

ANTIMONIURETTED HYDROGEN.

§ 291. The composition of this compound is not certainly known, since it has never been obtained perfectly free from hydrogen; it is, however, generally represented as SbH_3 . Antimoniuretted hydrogen is formed when antimony and hydrogen are brought in contact in the nascent state; this may be effected by pouring a solution of antimony into an apparatus from which hydrogen is evolved by zinc with dilute sulphuric acid; a mixture of hydrogen with antimoniuretted hydrogen is evolved, which is inodorous, insoluble in water, and burns with a livid flame, yielding water and teroxide of antimony; if a porcelain plate be depressed into the flame, a stain of finely-divided antimony will be deposited upon it; antimoniuretted hydrogen is decomposed when passed through a tube heated with a spirit-lamp, a shining mirror of metal being deposited immediately

¹ Reynoso has described a very ready method of preparing this reagent; it consists in precipitating a solution of terchloride of antimony by potassa, redissolving the precipitate in an excess of potassa, and adding permanganate of potassa until the solution acquires a pink color; it is then decolorized by a few drops of terchloride of antimony, evaporated, and allowed to crystallize; the crystals of bi-metantimoniate of potassa are washed with cold water. The same process may be employed for obtaining other metallic acids, as chromic and stannic acids.

before the flame. When passed into solution of nitrate of silver, antimoniu-retted hydrogen yields a black precipitate, the composition of which is not certainly known. Both the hydrogen and the metal are oxidized when the gas is passed into hot nitric acid.

The production of the hydrogen-compound of antimony is sometimes had recourse to in the detection of this metal, as will be further explained hereafter.

TERCHLORIDE OF ANTIMONY, $SbCl_3$ (*sesquichloride*, Sb_2Cl_3).

This compound was formerly known as *butter of antimony*, on account of its semi-solid consistence. It may be prepared by either of the following methods:—

I. By passing chlorine (slowly) over an excess of metallic antimony.

II. By distilling an intimate mixture of 1 part of powdered antimony and 2 parts of chloride of mercury (corrosive sublimate).

III. By dissolving tersulphide of antimony in hydrochloric acid:—



IV. By distilling a mixture of chloride of sodium and sulphate of teroxide of antimony.

V. By dissolving metallic antimony in hydrochloric acid, with gradual addition of nitric acid; too large a quantity of the latter must be avoided, since it will cause a precipitation of antimoniate of teroxide of antimony.

Properties.—Terchloride of antimony is a soft, gray solid, which deliquesces when exposed to air; it fuses at a gentle heat, and crystallizes on cooling in tetrahedra. It volatilizes at a moderately high temperature, yielding a vapor of sp. gr. 8.1. The terchloride dissolves, without alteration, in a small quantity of water, especially if a little acid be added, but a large quantity of water decomposes it, with formation of hydrochloric acid, and of a white precipitate, known as *powder of Alparoth*, which is an oxychloride of antimony, having the formula, $SbCl_3 \cdot 2SbO_3$, HO:—



When a solution of terchloride of antimony in acidulated water is poured into a large quantity of water, a very voluminous white precipitate is formed, which, after some time, contracts very considerably, and becomes converted into a collection of white prismatic needles, which are probably identical with those obtained by Pélilot, on adding hot water to a hydrochloric solution of the terchloride, which were found to have the composition $SbCl_3 \cdot 5SbO_3$. The above oxychlorides are both soluble in tartaric acid, and are converted, by long washing, into teroxide of antimony.

Nitric acid acts upon terchloride of antimony, producing the antimoniate of teroxide of antimony.

Terchloride of antimony is capable of absorbing ammoniacal gas, producing the compound, $SbCl_3 \cdot NH_3$.

It also combines with hydrochloric acid, and forms double chlorides with those of potassium, sodium and ammonium.

Terchloride of antimony is occasionally used in surgery; it also serves as a bronze for gun-barrels, upon which it deposits a film of metallic antimony.

PENTACHLORIDE OF ANTIMONY, $SbCl_5$.

Preparation.—The pentachloride is prepared by heating coarsely-powdered antimony in a retort of green glass, through which a stream of dry chlorine is passed; the neck of the retort is fitted into an adapter, which serves to condense the pentachloride; the product is to be completely saturated with chlorine, and

subsequently redistilled, the first portions, which contain the excess of chlorine, being rejected.

Properties.—Pentachloride of antimony is a yellowish liquid, which is volatile, and evolves thick white fumes when exposed to moist air; when brought in contact with water, energetic action takes place, and the pentachloride is first converted into a crystalline hydrate, and subsequently decomposed into hydrochloric and antimonic acids:—



When heated, the pentachloride is, to some extent, decomposed into terchloride and free chlorine.

Pentachloride of antimony is capable of combining with ammonia and with sulphuretted hydrogen.

A compound of pentachloride of antimony with chloride of sulphur has been obtained by the action of chlorine upon the tersulphide of antimony; this compound has the formula, $\text{SbCl}_5 \cdot 3\text{SCl}_2$; it is a white solid which decomposes, at a slightly elevated temperature, into chloride of sulphur, chlorine and terchloride of antimony.

Pentachloride of antimony is frequently employed in the laboratory as a chlorinating agent, since it readily yields chlorine to substances having a great affinity for it; thus, olefiant gas (C_2H_4), when passed through the pentachloride, is converted into Dutch liquid ($\text{C}_2\text{H}_2\text{Cl}_2$), and carbonic oxide into chlorocarbonic acid, the pentachloride being reduced to terchloride.

A chlorosulphide of antimony, SbCl_3S_2 , has been prepared by the action of hydrosulphuric acid upon pentachloride of antimony.

The *terbromide of antimony*, SbBr_3 , is a colorless crystalline solid.

The *teriodide* is a red solid.

The *terfluoride* forms colorless crystals.

The bromide iodide, and fluoride corresponding to antimonic acid are not known.

ANTIMONY AND SULPHUR.

Tersulphide	SbS_3 .
Pentasulphide	SbS_5 .

TERSULPHIDE OF ANTIMONY, SbS_3 .

§ 292. This sulphide is found pretty abundantly in nature, and forms the commonest ore of antimony (*gray ore of antimony*). It has a bluish-gray color and metallic lustre; is crystallized in prismatic needles, and has the sp. gr. 4.62. The native sulphide is generally associated with quartz, sulphate of baryta, or iron-pyrites. When heated in close vessels, it fuses easily, without suffering any decomposition,¹ and crystallizes on cooling. It is volatile, and may be sublimed unchanged. When heated with access of air, it is partially converted into teroxide, which remains in combination with unaltered tersulphide. When heated to redness in a current of hydrogen, it is reduced to metallic antimony.

The tersulphide of antimony dissolves in hydrochloric and sulphuric acids, with the aid of heat, sulphuretted hydrogen being evolved; it dissolves to a considerable extent in nitric acid, leaving a white residue.

This sulphide plays the part of a sulphur-acid, dissolving readily in the alkaline sulphides. It is also soluble in the caustic alkalies, producing compounds

¹ This property is taken advantage of in order to free the crude sulphide from gangue.

of the alkali with teroxide of antimony, and of an alkaline sulphide with tersulphide of antimony; thus:—



Anhydrous tersulphide of antimony may be obtained artificially, in prismatic crystals with metallic lustre, by fusing a mixture of sulphur with antimoniate of teroxide of antimony, when sulphurous acid is evolved.

The *hydrated tersulphide* is obtained as a fine orange-red precipitate, when sulphuretted hydrogen is passed through a solution of teroxide of antimony; it loses its water when moderately heated, assuming a dark gray color, and metallic lustre.

Tersulphide of antimony is occasionally used for the preparation of pure hydrosulphuric acid. Its chief application is in pyrotechny and in the preparation of detonating compositions for military purposes. The latter use depends upon its combustibility, and the former upon the property which it possesses of burning with a bright bluish-white flame.

The compounds known as *glass of antimony*, *liver of antimony*, and *crocus*, are formed by roasting the native tersulphide with access of air. They contain variable proportions of teroxide and tersulphide of antimony.

Glass of antimony contains about eight parts of teroxide, and one part of tersulphide; it is transparent, and of a reddish-yellow color.

Crocus has a similar color, but is opaque; it contains eight parts of teroxide and two of tersulphide; *liver of antimony* has an opaque brown color, and contains about half its weight of tersulphide of antimony.

These compounds are chiefly employed in veterinary medicine, and in the preparation of tartar-emetic.

PENTASULPHIDE OF ANTIMONY, SbS_5 (*Sulphantimonic acid*).

This sulphide is obtained by passing sulphuretted hydrogen through a solution of pentachloride of antimony in hydrochloric acid. It forms a bright orange-red precipitate, which is a hydrate of the pentasulphide; when heated, it first loses its water, and afterwards two equivalents of sulphur, leaving the tersulphide of antimony.

Pentasulphide of antimony is a powerful sulphur-acid, and is capable of expelling hydrosulphuric acid from the hydrosulphates of alkaline sulphides.

The *sulphantimoniate of sulphide of sodium*, 3NaS.SbS_5 , is sometimes employed in medicine; it is prepared by intimately mixing 18 parts of tersulphide of antimony, 12 parts of carbonate of soda (dry), 13 parts of lime, and $3\frac{1}{2}$ parts of sulphur; the mixture is well triturated for half an hour, then digested, with frequent agitation, for two or three days, in a flask perfectly filled with cold water; the filtered solution is then evaporated, first on a sand-bath, then in the receiver of an air-pump, when tetrahedral crystals are obtained, of the formula $3\text{NaS.SbS}_5.18\text{H}_2\text{O}$; these are colorless, or slightly yellow, and very soluble in water; acids precipitate the sulphantimonic acid from this solution.

KERMES MINERAL.—The pharmaceutical compound known under this name is a mixture of teroxide and tersulphide of antimony, which is prepared, either by fusing tersulphide of antimony with carbonate of soda, and boiling the fused mass with much water, or by boiling the finely powdered tersulphide with carbonate of soda and a large quantity of water; in either case, the liquid, filtered while hot, deposits the kermes on cooling; this substance is collected on a filter, well washed, and dried at a low temperature.

The formation of kermes is easily explained; the tersulphide of antimony is decomposed by the soda, yielding sulphide of sodium and teroxide of antimony, which combines with part of the soda:—



whilst a portion of unaltered tersulphide of antimony dissolves in the sulphide of sodium; since the compound of teroxide of antimony with soda is decomposed by boiling with water, and tersulphide of antimony is more soluble in a hot than in a cold solution of sulphide of sodium, a mixture of the teroxide and tersulphide would of course be deposited as the solution cools. The kermes generally contains a small quantity of sulphide of sodium, carried down with the tersulphide of antimony, which serves to account for the variation of color observed in different specimens of this preparation. The crystalline teroxide of antimony may be recognized in kermes under the microscope.

When the mother-liquors from which the kermes has been deposited are treated with dilute sulphuric acid, a mixture of tersulphide and pentasulphide of antimony, known as *golden sulphuret of antimony*, is deposited.

§ 293. ALLOYS OF ANTIMONY.—Antimony is capable of forming alloys with many metals; it has already been said that this metal is employed to harden several useful alloys.

An alloy of antimony and potassium is obtained by heating, in a covered crucible, for some hours, a mixture of 6 parts of tartar-emetic with 1 part of nitre, when a button containing a considerable quantity of antimony is obtained, which decomposes water at the ordinary temperature, with disengagement of hydrogen.

If the alloy be prepared in a very fine state of division, by calcining, for three hours, in an earthen crucible, a mixture of 100 parts of tartar-emetic, and 3 parts of lampblack, it will be found capable of taking fire, with explosion, in moist air; it should therefore be allowed to cool, in a closed crucible, beneath a bell-jar of dry air, and must be handled with great care.

An alloy of antimony with iron (*Réaumur's alloy*) may be procured by fusing, at a very high temperature, a mixture of 7 parts of antimony and 3 of iron filings; the alloy is exceedingly hard, and emits sparks when filed.

METALLURGY OF ANTIMONY.

§ 294. *Metallic antimony*, associated with small quantities of silver and iron, has been found in nature.

Antimony exists most frequently in combination with sulphur, and indeed, the only ore of antimony, in a strict sense, is the *gray ore*, or native tersulphide.

A mineral containing antimony and nickel, and termed *nickeliferous sulphuret of antimony* or *nickel-antimony*, is known.

Antimony is sometimes, though rarely, found in an oxidized state in *white ore of antimony*, *ochre of antimony*, and *red ore*, which last appears to be an oxy-sulphide.

The reduction of antimony from the ore consists of two distinct processes, one of which is intended to separate the ore from the gangue, and the other to obtain the antimony in the metallic state.

The former object is attained by fusing the crude ore upon the inclined hearth of a reverberatory furnace, when the tersulphide fuses, and flows away from the gangue into appropriate receptacles.

The purified ore is afterwards roasted in a reverberatory furnace, where it is converted into oxy-sulphide of antimony (glass of antimony). This is powdered, and mixed with $\frac{1}{2}$ its weight of charcoal previously saturated with a strong solution of carbonate of soda; on heating this mixture in a crucible, the teroxide of antimony is reduced by the charcoal, and a portion of the tersulphide, having been converted into teroxide by double decomposition with the soda of the carbonate, is also reduced; a quantity of regulus of antimony is found at the bottom of the crucible, and, above it, a slag containing tersulphide and teroxide of antimony, which may be employed for the preparation of kermes mineral.

The tersulphide of antimony was formerly reduced by iron at a high temper-

ture, but it was found necessary to give up this process, since the metal obtained was always alloyed with a large quantity of iron.

Assay of Ores of Antimony.—Ores of antimony which do not contain sulphur are assayed by fusion with 3 parts of black flux, a very high temperature being avoided, because of the volatility of the metal. Care must be taken that the button be not broken in extracting it from the crucible.

The best method of assaying the sulphide of antimony consists in fusing it at a moderate heat, in an earthen crucible, with 4 parts of Liebig's cyanide of potassium.

It is obvious that the volatility of the metal must prevent the attainment of anything more than an approximation to the amount of antimony present in the ore.

§ 295. *Pharmaceutical Preparations of Antimony.*—Several preparations of antimony are used in medicine.

The most important of these is *tartar-emeti*c, the double tartrate of antimony and potassa, the description of which falls within the province of organic chemistry.

Antimonium calcinatum, or *diaphoretic antimony*, is prepared by deflagrating the tersulphide with 3 parts of nitre, and washing the fused mass with water; the residue contains an acid antimoniate of potassa.

Antimonii cinis (*antimony-ash*) is an oxy-sulphide, prepared by roasting the tersulphide in air.

The substance termed *antimonii oxydum*, or *antimonii oxydum nitro-muriaticum*, is prepared by dissolving the tersulphide in hydrochloric or nitro-hydrochloric acid, precipitating by water, and washing the precipitate as long as the washings have any acid reaction; it consists of teroxide of antimony with a little terchloride.

ARSENIC.

Sym. As. Eq. 75. Sp. Gr. 5.75.

§ 296. Although, in its combinations, this element more nearly resembles the non-metallic bodies, we have, according to the usual custom, placed it among the metals.

Arsenic is rather widely diffused in nature, sometimes in the metallic state, or as a sulphide, but generally associated with the ores of iron, nickel, cobalt, and copper.

The mineral known as *arsenical pyrites* (*mispickel*) usually contains arsenic, iron, and sulphur, in the proportions expressed by the formula FeS_2 , FeAs_2 .

Red and yellow orpiment will be spoken of under the sulphides of arsenic.

Preparation.—Arsenic is prepared either from *mispickel* or from arsenious acid.

The arsenical pyrites is strongly heated in earthen cylinders, with fragments of iron, which retain the whole of the sulphur, while the arsenic sublimes into other cylinders, serving as receivers; it is purified by redistilling with a little charcoal.

In order to obtain arsenic from arsenious acid, it is only necessary to mix the latter with about twice its weight of black flux, and to heat the mixture in a Hessian crucible, which is covered with a second crucible, kept cool in order that the arsenic may be condensed; the two crucibles should be luted together, a small aperture being left for the escape of the carbonic oxide.

Properties.—Arsenic has a steel-gray color, and metallic lustre; it is crystal-

line in texture, and exceedingly brittle. It is converted into vapor at about 572° F. (300° C.), without previously fusing; it may, however, be fused in a sealed tube. If the vapor of arsenic be allowed to condense slowly, the metal is deposited in brilliant rhombohedral crystals. The density of the vapor of arsenic is 10.39.

When exposed to air, arsenic is tarnished and assumes a dull black color, probably becoming covered with a film of suboxide; when placed in contact with water, air being allowed free access, it is gradually converted into arsenious acid.

When heated in air, this metal is oxidized, and produces white fumes of arsenious acid, at the same time exhaling a peculiar alliaceous odor, ascribed by some to the vapor of the metal itself, by others to a suboxide of arsenic.

Arsenic burns, when heated in oxygen, with a pale blue flame, producing arsenious acid. It is not capable of decomposing water at any temperature, nor in presence of acids.

Arsenic is not attacked by hydrochloric acid, but nitric acid dissolves it readily, arsenious or arsenic acid being produced, according to the concentration of the acid; when the ordinary nitric acid of the laboratory is employed, the former is usually found in solution. Chlorine combines energetically with arsenic, the powdered metal taking fire spontaneously in this gas.

Metallic arsenic does not produce symptoms of poisoning in animals till a considerable period after its administration; it is probably first converted into arsenious acid.

The substance known as *fly-powder* consists of a mixture of metallic arsenic with arsenious acid, and is prepared by exposing the metal to air in presence of water.

Arsenic exhibits in its combinations a remarkable similarity to phosphorus; thus, with hydrogen, oxygen, and chlorine, it forms compounds analogous to those formed by that element.

ARSENIC AND OXYGEN.

Arsenious acid	AsO ₂
Arsenic acid	AsO ₃ ¹

§ 297. The existence of an inferior oxide is regarded as doubtful; some chemists contend that the product of the slow oxidation of arsenic by exposure to moist air, is merely a mixture of metallic arsenic and arsenious acid; it certainly yields these products when subjected to heat.

ARSENIOUS ACID, AsO₂ (*commonly called ARSENIC, or White Arsenic.*)

Preparation.—Arsenious acid is prepared by roasting arsenical pyrites with free access of air, when the arsenic is oxidized, and the arsenious acid is condensed in large chambers.

It is also obtained as a by-product in roasting certain ores, especially those of tin and cobalt.

The arsenious acid thus obtained is purified by sublimation.

Properties.—Arsenious acid, when freshly prepared, forms transparent colorless, vitreous masses, which, after some time, become opaque externally, the opacity afterwards extending throughout the mass, until it resembles a fragment of porcelain.

¹ The equivalent of arsenic is sometimes considered as 37.5, when *arsenious acid* would be As₂O₃, and *arsenic acid* As²O₅.

The vitreous and opaque varieties of arsenious acid differ considerably in some of their properties.

The specific gravity of the vitreous acid is 3.74, that of the opaque variety 3.70.

When the vitreous acid is reduced to powder, it is converted into the opaque variety.

At the ordinary temperature, the vitreous acid is three times as soluble in water as that which is opaque.

Heat is capable of causing the opaque acid to become vitreous, while cold reverses the change; hence, by long boiling with water, the opaque acid is converted into the vitreous modification, and, as the solution cools, part of the arsenious acid in the opaque condition is deposited; thus these two forms of arsenious acid are generally found in the same solution.

When vitreous arsenious acid is dissolved in boiling dilute hydrochloric acid, it is deposited on cooling in regular octohedra of the opaque variety, the deposition of each crystal being said to be attended by a flash of light, which is not the case if the crystals be redissolved in hydrochloric acid, or if the opaque variety be originally employed.

Arsenious acid is dimorphous, and has been obtained by sublimation in thin prisms. It volatilizes below a red heat, without previously fusing; it may, however, be fused, if heated in a sealed tube.

Vapor of arsenious acid is inodorous, and has the specific gravity 13.85. If it be condensed in a receiver which attains a pretty high temperature, a layer of vitreous arsenious acid is formed, whilst, if deposited in a slow current of air, the acid is obtained in fine octohedral crystals.

Arsenious acid is sparingly soluble in cold water, but, as implied above, more so in hot water; 1000 parts of boiling water dissolve about 80 parts of arsenious acid, and the solution, after cooling to 60° F. (15°.5 C.), retains only 30 parts. If water at 60° F. be mixed with arsenious acid in powder, only 2½ parts are dissolved by 1000 of water.¹

The aqueous solution has a feeble acid reaction to test-papers. It is much more soluble in hydrochloric acid. When arsenious acid is boiled with concentrated hydrochloric acid, terchloride of arsenic is formed and volatilized.

When boiled with nitric (or better, nitro-hydrochloric) acid, arsenious is converted into arsenic acid. Solution of ammonia is capable of dissolving it, and of depositing it again in crystals. Arsenious acid is easily reduced to the metallic state by hydrogen or carbon at a high temperature.

This acid is bibasic, forming salts, which are termed arsenites. It is a most virulent poison.

Uses.—Arsenious acid is used in the manufacture of glass, where it serves to oxidize any (prot-) oxide of iron which may be present, converting it into sesquioxide, which does not color the glass so deeply. It also enters into the composition of various pigments and coloring matters. Arsenious acid is extensively employed for destroying vermin, and for preventing the smut in grain.

§ 298. *Arsenite of Potassa* (2KO.AsO₂) is obtained by dissolving arsenious acid in solution of potassa.

It crystallizes with difficulty, and is deliquescent; its solution has an alkaline reaction.²

¹ The amount dissolved, however, depends, to a remarkable extent, upon the duration of the contact between the arsenious acid and the water.

² According to Pasteur, there exist two other arsenites of potassa, KO.HO.2AsO₂, and KO.AsO₂.

Rose has obtained insoluble arseniates of magnesia and the alkalis, by fusing ignited arseniate of magnesia and ammonia with alkaline carbonates.

ARSENITE OF COPPER, $2\text{CuO} \cdot \text{AsO}_2$. (*Scheele's green*.)

This substance is precipitated in a hydrated state when sulphate of copper is added to a solution of a neutral arsenite.

It is prepared on the large scale by dissolving $6\frac{1}{2}$ lbs. of carbonate of potassa and $2\frac{1}{2}$ lbs. of arsenious acid in 3 gallons of water, and gradually adding the liquid to a boiling solution of $6\frac{1}{2}$ lbs. of sulphate of copper in 9 gallons of water, with continual stirring.

The shade of color may be modified by varying the quantity of arsenious acid.

Arsenite of copper dissolves readily in acids, and in ammonia. When heated, the arsenious acid is expelled, oxide of copper being left. It is a very active poison.

Uses.—Scheele's green is employed largely by paper-stainers, and in oil-painting. It is also used to a lamentable extent in coloring ornaments of confectionery, and grave accidents frequently arise from this cause.

The pigment known as *Schweinfurt green* is a compound of arsenite with acetate of copper, $\text{CuO} \cdot \text{A} \cdot 3(2\text{CuO} \cdot \text{AsO}_2)$, and is prepared by mixing together boiling solutions of equal weights of arsenious acid and of acetate of copper, the ebullition being maintained for some time after mixing.

ARSENIC ACID, AsO_5 .

§ 299. *Preparation*.—Arsenious acid is heated with a considerable excess of nitric acid and a small quantity of hydrochloric; 8 parts of arsenious acid may be dissolved in 24 parts of nitric, and 2 parts of hydrochloric acid. The solution is evaporated to a syrupy consistence, and pretty strongly heated, to expel the excess of acid.

Properties.—Arsenic acid is a white deliquescent solid; when strongly heated, it first fuses, and is decomposed into arsenious acid and oxygen. This acid is very soluble in water, but dissolves slowly after it has been dried; the aqueous solution deposits crystals if sufficiently evaporated, and set aside. These crystals contain hydrated arsenic acid. It is easily decomposed by deoxidizing agents; sulphurous acid reduces it to arsenious acid.

Arsenic acid is tribasic; its salts much resemble those of the tribasic phosphoric acid with which it is isomorphous; like these latter, the arseniates may contain 1 or 2 eqs. of basic water.

Tribasic arseniate of potassa, with 3 eqs. of fixed base ($3\text{KO} \cdot \text{AsO}_5$), is prepared by adding an excess of potassa to arsenic acid, and crystallizes in fine deliquescent needles.

Common arseniate of potassa ($2\text{KO} \cdot \text{HO} \cdot \text{AsO}_5$) is prepared by neutralizing potassa with arsenic acid; it is deliquescent, and has not been crystallized.

Acid arseniate of potassa, $\text{KO} \cdot 2\text{HO} \cdot \text{AsO}_5$, may be obtained by adding an excess of arsenic acid to the preceding salt; it crystallizes in forms derived from the octohedron, and is unaltered in air.

The corresponding *arseniates of soda* have been obtained.

The common arseniate, $2\text{NaO} \cdot \text{HO} \cdot \text{AsO}_5$, crystallizes with 26 eqs. of water; the crystals effloresce in air.

Solutions of the arseniates give, with nitrate of silver, a brick-red precipitate of the *tribasic arseniate of silver*, $3\text{AgO} \cdot \text{AsO}_5$, the solution being neutral or acid after the reaction, according to the amount of fixed base present.

Arsenic acid is capable of forming insoluble compounds with binoxide of tin, as may be shown by oxidizing an alloy of tin and arsenic with nitric acid, when a considerable quantity of arsenic may be found in the residue.

ARSENIURETTED HYDROGEN, AsH_3 .

§ 300. This compound is prepared by dissolving an alloy of tin and arsenic in hydrochloric acid, with the aid of heat; or by acting upon zinc with dilute sulphuric acid in presence of arsenic. The gas obtained by these methods always contains free hydrogen.

Properties.—Arseniuretted hydrogen is a colorless gas having a sickly alliaceous odor; its sp. gr. is 2.69. It may be liquefied at $-22^\circ F.$ ($-30^\circ C.$) It is somewhat soluble in water; 5 vols. of water dissolve about 1 vol. of the gas. Arseniuretted hydrogen is inflammable, and burns with a livid flame, yielding arsenious acid and water; if it be burnt in a bell-jar, with a limited supply of air, a brown deposit (said to be a solid compound of arsenic with hydrogen) is formed simultaneously with the above products. A similar brown deposit is formed when the gas is kept for a long time over water.

If a porcelain plate be depressed into the flame of arseniuretted hydrogen, so as partially to cut off the supply of air, the hydrogen alone is oxidized, and a spot of arsenic is deposited upon the porcelain.

This gas is very readily decomposed into its elements by heat; if the tube through which arseniuretted hydrogen is passed be heated to redness with a spirit-lamp, a lustrous mirror of metallic arsenic is deposited at some distance from the heated portion.

Chlorine decomposes arseniuretted hydrogen with great energy, emitting a brilliant light. The gas is absorbed by several metallic salts (sulphate of copper, nitrate of silver, &c.), producing, in some cases, dark precipitates, the nature of which is not known with certainty.

It is a very poisonous gas, and great care should be taken not to respire it.

Arseniuretted hydrogen is sometimes prepared in order to furnish indications of the presence of arsenic (Marsh's test); we defer the details of the process until the detection of arsenic comes under consideration.

TERCHLORIDE OF ARSENIC, $AsCl_3$.

To prepare this substance, arsenic is gently heated in a retort, through which a current of dry chlorine is passed; or it may be obtained by distilling the metal with 6 parts of chloride of mercury (corrosive sublimate).

It is a colorless liquid, heavier than water, and boiling at $270^\circ F.$ ($132^\circ C.$) The density of its vapor is 6.3.

Terchloride of arsenic is decomposed by water, yielding hydrochloric and arsenious acids:—¹



It is said to be poisonous.

No pentachloride of arsenic has yet been obtained.

A compound of terchloride of arsenic with 3 eqs. of chloride of sulphur has been obtained.

ARSENIC AND SULPHUR.

Subsulphide	As_2S
Bisulphide	As_2S_2
Tersulphide	As_2S_3
Pentasulphide	As_2S_5
Octodeca-sulphide	As_2S_{12}

¹ A hydrated terchloride of arsenic is produced when the terchloride is mixed with a small quantity of water, or when arsenious acid is dissolved in hydrochloric acid.

§ 301. *Sulphide of arsenic* (As_2S_3) is obtained by digesting realgar with a concentrated solution of potassa; it is a dark brown insoluble substance, which takes fire when moderately heated in air.

BISULPHIDE OF ARSENIC, RED ORPIMENT, REALGAR, As_2S_2 .

This substance is found in nature crystallized in oblique rhombic prisms.

It may be prepared by fusing 1 eq. of metallic arsenic with 2 eqs. of sulphur, or 2 eqs. of arsenious acid, with 5 eqs. of sulphur.

Realgar is a soft mineral of a fine brownish-red color; when heated, it fuses, and may be sublimed unchanged. It is insoluble in water, but dissolves in nitric acid.

The bisulphide of arsenic is a sulphur-acid, forming salts with the sulphur-bases. When treated with potassa, it yields arsenite of potassa, subsulphide of arsenic, As_2S_3 , which is precipitated, and a soluble compound of bisulphide of arsenic with sulphide of potassium. It is soluble in ammonia.

Realgar is chiefly employed as a pigment; it is also useful in pyrotechny; the well-known *Indian fire*, which burns with such a brilliant white light, is composed of 2 parts of realgar, 24 parts of nitre, and 7 parts of flowers of sulphur.

TERSULPHIDE OF ARSENIC, KING'S YELLOW, YELLOW ORPIMENT, SULPHARSENIOUS ACID, As_2S_5 .

The tersulphide is found in nature in beautiful crystalline plates, of a brilliant yellow color, and generally mixed with arsenious acid. It may be artificially obtained by distilling arsenic or arsenious acid with sulphur:—



or by passing sulphuretted hydrogen through a solution of arsenious acid acidulated with hydrochloric acid. This precipitate is a hydrate.

Tersulphide of arsenic has always a fine yellow color; when heated in close vessels, it first fuses, then sublimes. Heated in contact with air, it burns with a pale flame, and is converted into arsenious and sulphurous acids.

The tersulphide is scarcely affected by hydrochloric acid, but dissolves readily in nitric acid and in ammonia.

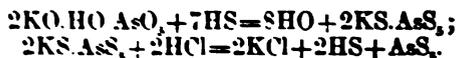
It is a powerful sulphur-acid; the alkalis and their carbonates (the latter with evolution of carbonic acid) dissolve it, forming arsenites and *sulpharsenites*:—



Of course, it dissolves easily in alkaline sulphides. Tersulphide of arsenic is poisonous. It is used in dyeing; in order to fix orpiment and realgar in the fibre of the fabric, they are dissolved in ammonia, and thus applied; as the solvent evaporates, the coloring matter is precipitated.

PENTASULPHIDE OF ARSENIC, SULPHARSENIC ACID, As_2S_5 .

This compound may be prepared by treating with hydrosulphuric acid a solution of arsenic acid mixed with hydrochloric acid; however, since the precipitate does not deposit till after a considerable period, it is more convenient to saturate a solution of arseniate of potassa (2KO.HO.AsO_3) with sulphuretted hydrogen, and to decompose the resulting sulpharseniate of sulphide of potassium (2KS.AsS_3) with hydrochloric acid:—



Pentasulphide of arsenic is a yellow solid, which fuses a little above the boiling-point of water, and acquires a reddish color; it may be sublimed unchanged.

The pentasulphide much resembles the tersulphide in solubility, but is a more powerful sulphur-acid; it expels carbonic acid from alkaline carbonates, hydrosulphuric acid from the hydrosulphates of alkaline sulphides, and forms well-defined sulphur-salts.

There exist *sulpharseniates of the sulphides of potassium, sodium, and ammonium*, containing respectively 6, 2, and 3 eqs. of the sulphide of either of these metals, in combination with sulpharsenic acid; they are prepared by passing sulphuretted hydrogen through the arseniates with 1, 2, and 3 equivalents of fixed base.

Octodeca-sulphide of Arsenic.—Berzelius obtained a sulphide of arsenic of the formula AsS_{18} , by precipitating with alcohol a neutral solution of sulpharseniate of sulphide of potassium, filtering, and evaporating two-thirds of the alcohol added, when the new compound was obtained in brilliant yellow crystals.

ARSENIC WITH METALS.—Arsenic combines directly with several metals; the *arsenide of manganese*, formed by the combination of its elements at a red heat, is a hard gray substance with metallic lustre. It burns in air with a bluish flame and alliaceous odor; it may be represented by Mn_2As .

Arsenic and iron are capable of combining in several proportions, forming compounds which are harder, more brittle, and more fusible than iron itself.

The *arsenides of iron* are found in nature. The compound $FeAs$ occurs in some specimens of iron-pyrites.

Fe_2As_3 usually constitutes the mineral termed *arsenical iron*.

$FeAs_2$ exists in mispickel, the composition of which may be expressed by $FeS_2, FeAs_2$.

Arsenides of nickel, having the composition $NiAs$ and $NiAs_2$, are natural products.

Subarsenide of cobalt, having the composition Co_2As_3 , is obtained when arseniate of cobalt is reduced by hydrogen.

Several compounds of arsenic and cobalt exist in the mineral kingdom; the chief of these are $CoAs$ and Co_2As_3 . The latter loses arsenic when heated in close vessels.

In the natural sesqui-arsenide of cobalt, part of the latter is often replaced by iron and nickel.

Pure gray cobalt-ore (Tunaberg cobalt) may be expressed by the formula $CoAs_2, CoS_2$.

Cobalt-glance contains $CoAs, CoS_2$.

Arsenic and Copper.—A very small quantity of arsenic suffices to bleach copper and to render it brittle, as may be seen by heating this metal in the vapor of arsenic.

A compound of the formula Cu_3As (*white tombac*), is obtained when copper-filings are heated with an equal weight of arsenic. Cu_3As is prepared by the action of arseniuretted hydrogen upon a salt of copper.¹

Arsenic and Tin.—Tin is rendered harder, less malleable, and highly crystalline when alloyed with a small quantity of arsenic (*see speculum-metal*, p. 389).

These metals may be made to unite directly in almost any proportion, forming gray brittle compounds, less fusible than tin, and easily oxidized by roasting. When they are treated with hydrochloric acid, a mixture of hydrogen and arseniuretted hydrogen is disengaged, and a little arsenic liberated at the same time.

Pharmaceutical Preparations of Arsenic.—Some compounds of arsenic are occasionally used in medicine and surgery.

The *arsenical caustic* employed in cancer is prepared by fusing arsenious acid with tersulphide of antimony.

¹ *Condurrite* is a mixture of suboxide of copper, arsenious acid, and the residue of the mineral by the alteration of which it has been originally formed; according to Blyth, the original mineral would have the formula Cu_4As .

Arsenious acid in the pure state, is also sometimes made use of, but it is more generally employed in the form of "*liquor arsenicalis*," which is a solution of arsenite of potassa, prepared by dissolving arsenious acid in carbonate of potassa.

The sulphides of arsenic have also been employed as external applications.

TUNGSTEN.

Sym. W. Eq. 95. Sp. Gr. 17.6.

§ 302. This metal, which is by no means very abundant in nature, is found chiefly in the mineral *wolfram*, which contains tungstic acid in combination with the oxides of iron and manganese.

Preparation.—Tungsten may be obtained by reducing tungstic acid with dry hydrogen at a high temperature, when the metal is left in a finely-divided state.

It is procured in a coherent (but not fused) mass, by strongly heating tungstic acid in a crucible lined with charcoal.

Properties.—This metal has a dark gray color, and a metallic lustre when rubbed; its hardness is very considerable; it is not affected by air at the ordinary temperature, but, when heated to redness, is oxidized, and converted into tungstic acid. It is not volatile and nearly infusible. It is not affected by water at the ordinary temperature, but at high temperatures decomposes it, liberating hydrogen, and forming tungstic acid.

Hydrochloric and dilute sulphuric acids do not act upon this metal; concentrated sulphuric acid, with the aid of heat, oxidizes it; nitric acid readily converts it into tungstic acid.

When fused with hydrated alkalis, it is converted into a tungstate, hydrogen being disengaged; fused nitrate of potassa converts it into tungstate of potassa.

Tungsten combines directly with chlorine, but not with sulphur.

TUNGSTEN AND OXYGEN.

Binoxide of tungsten	WO ₂ .
Tungstic acid	WO ₃ .

An intermediate oxide also exists.

BINOXIDE OF TUNGSTEN, WO₂.

This oxide may be obtained by reducing tungstic acid with hydrogen at a carefully regulated temperature, or by moistening that compound with hydrochloric acid, and placing it in contact with zinc.

A better method consists in fusing 1 part of wolfram with 2 parts of carbonate of soda, in a platinum crucible, extracting the tungstate of soda from the fused mass with water, mixing the solution with $\frac{1}{2}$ part of chloride of ammonium, evaporating to dryness, and calcining the residue; a mixture of chloride of sodium with binoxide of tungsten is thus obtained, from which the former may be extracted with water; the binoxide should be digested with a little potassa to remove the last traces of tungstic acid.

Binoxide of tungsten is a dark brown powder, insoluble in water and acids; when boiled with solution of potassa, it yields tungstate of potassa, hydrogen being disengaged. When heated in air, binoxide of tungsten is converted into tungstic acid.

Binoxide of tungsten is an indifferent oxide.

A compound of this oxide with soda, having the formula $\text{NaO} \cdot 2\text{WO}_3$,¹ is obtained when acid tungstate of soda is reduced, at a red heat, by hydrogen; if the resulting mass be treated with water, neutral tungstate of soda is dissolved, and the new compound is obtained in brilliant, yellow cubical crystals; it should be washed, first with hydrochloric acid, then with an alkali, to free it from tungstic acid.

This compound is remarkable (among soda-compounds) for its insolubility in water and acids.

TUNGSTIC ACID, WO_3 .

This acid is generally prepared from the mineral *wolfram*, which may be represented by the general formula $\text{FeO} \cdot \text{WO}_3 + \text{MnO} \cdot \text{WO}_3$, the proportions of the two tungstates varying in different specimens.

This mineral forms dark brown quadrilateral prisms, with considerable lustre.

In order to prepare tungstic acid, wolfram is treated with nitro-hydrochloric acid, which dissolves the oxides of iron and manganese, leaving tungstic acid; the residue is collected on a filter, well washed, and treated with ammonia, which dissolves the tungstic acid, leaving behind any silicious matters which may be present.

The tungstate of ammonia may be crystallized from this solution, and heated in air, when tungstic acid is left.

Tungstic acid is a solid of a straw-yellow color; when heated, it is converted into a blue *intermediate oxide*, $\text{WO}_2 \cdot \text{WO}_3$, which is always the product of a partial reduction of this acid.

Tungstic acid is insoluble in water and acids; when prepared by the above method, it is not easily soluble in alkalis, but if it be obtained by decomposing an alkaline tungstate with hydrochloric acid, it dissolves readily in solutions of the fixed alkalis and of ammonia.

Tungstic acid is capable of existing in several modifications, which bear to each other a relation similar to that between stannic and metastannic acids.²

Only the *tungstates of potassa, soda, and ammonia* are soluble in water. These salts are composed of single equivalents of acid and base.

The tungstates are decomposed by acids, being converted, first into acid tungstates, and ultimately into pure tungstic acid.

Solutions of the neutral tungstates of the alkalis are not precipitated by sulphuretted hydrogen, a soluble sulphur-salt being produced.

When tungstic acid, or a tungstate, is placed in contact with hydrochloric acid and zinc, the blue intermediate oxide of tungsten is obtained.

The tungstates of soda and lime have recently been applied in dyeing.

Tungstic acid combines with the strong mineral acids, forming sparingly-soluble compounds.

CHLORIDES OF TUNGSTEN.

The *bichloride* (WCl_2) is obtained by passing chlorine over tungsten heated in a tube; it forms small dark red needles, which are very fusible and volatile; it is decomposed by water.

The *trichloride* (WCl_3), also red, crystalline, and decomposed by water, is formed when sulphotungstic acid is heated in a current of chlorine. Its vapor has a red-brown color.

When chlorine is passed over tungstic acid, an oxychloride is obtained, of the formula $\text{WO}_2 \cdot \text{Cl}$; it forms yellow needles.

¹ Wright has obtained this compound by the action of other reducing agents upon bi-tungstate of soda; he assigns to it the formula $\text{WO}_2 \cdot \text{WO}_3 \cdot \text{NaO} \cdot \text{WO}_3$.

² Laurent, *Ann. Ch. Phys.* [3] xli. 54.

Arsenious acid in the pure state, is also sometimes made use of, but it is more generally employed in the form of "*liquor arsenicalis*," which is a solution of arsenite of potassa, prepared by dissolving arsenious acid in carbonate of potassa. The sulphides of arsenic have also been employed as external applications.

TUNGSTEN.

Sym. W. Eq. 95. Sp. Gr. 17.6.

§ 802. This metal, which is by no means very abundant in nature, is found chiefly in the mineral *wolfram*, which contains tungstic acid in combination with the oxides of iron and manganese.

Preparation.—Tungsten may be obtained by reducing tungstic acid with dry hydrogen at a high temperature, when the metal is left in a finely-divided state.

It is procured in a coherent (but not fused) mass, by strongly heating tungstic acid in a crucible lined with charcoal.

Properties.—This metal has a dark gray color, and a metallic lustre when rubbed; its hardness is very considerable; it is not affected by air at the ordinary temperature, but, when heated to redness, is oxidized, and converted into tungstic acid. It is not volatile, and nearly infusible. It is not affected by water at the ordinary temperature, but at high temperatures decomposes it, liberating hydrogen, and forming tungstic acid.

Hydrochloric and dilute sulphuric acids do not act upon this metal; concentrated sulphuric acid, with the aid of heat, oxidizes it; nitric acid readily converts it into tungstic acid.

When fused with hydrated alkalis, it is converted into a tungstate, hydrogen being disengaged; fused nitrate of potassa converts it into tungstate of potassa. Tungsten combines directly with chlorine, but not with sulphur.

TUNGSTEN AND OXYGEN.

Binoxide of tungsten	WO_2 .
Tungstic acid	WO_3 .

An intermediate oxide also exists.

BINOXIDE OF TUNGSTEN, WO_2 .

This oxide may be obtained by reducing tungstic acid with hydrogen at a carefully regulated temperature, or by moistening that compound with hydrochloric acid, and placing it in contact with zinc.

A better method consists in fusing 1 part of wolfram with 2 parts of carbonate of soda, in a platinum crucible, extracting the tungstate of soda from the fused mass with water, mixing the solution with $\frac{1}{2}$ part of chloride of ammonium, evaporating to dryness, and calcining the residue; a mixture of chloride of sodium with binoxide of tungsten is thus obtained, from which the former may be extracted with water; the binoxide should be digested with a little potassa to remove the last traces of tungstic acid.

Binoxide of tungsten is a dark brown powder, insoluble in water and acids; when boiled with solution of potassa, it yields tungstate of potassa, hydrogen being disengaged. When heated in air, binoxide of tungsten is converted into tungstic acid.

Binoxide of tungsten is an indifferent oxide.

A compound of this oxide with soda, having the formula $\text{NaO} \cdot 2\text{WO}_3$,¹ is obtained when acid tungstate of soda is reduced, at a red heat, by hydrogen; if the resulting mass be treated with water, neutral tungstate of soda is dissolved, and the new compound is obtained in brilliant, yellow cubical crystals; it should be washed, first with hydrochloric acid, then with an alkali, to free it from tungstic acid.

This compound is remarkable (among soda-compounds) for its insolubility in water and acids.

TUNGSTIC ACID, WO_3 .

This acid is generally prepared from the mineral *wolfram*, which may be represented by the general formula $\text{FeO}, \text{WO}_3 + \text{MnO}, \text{WO}_3$, the proportions of the two tungstates varying in different specimens.

This mineral forms dark brown quadrilateral prisms, with considerable lustre.

In order to prepare tungstic acid, wolfram is treated with nitro-hydrochloric acid, which dissolves the oxides of iron and manganese, leaving tungstic acid; the residue is collected on a filter, well washed, and treated with ammonia, which dissolves the tungstic acid, leaving behind any silicious matters which may be present.

The tungstate of ammonia may be crystallized from this solution, and heated in air, when tungstic acid is left.

Tungstic acid is a solid of a straw-yellow color; when heated, it is converted into a blue *intermediate oxide*, WO_2, WO_3 , which is always the product of a partial reduction of this acid.

Tungstic acid is insoluble in water and acids; when prepared by the above method, it is not easily soluble in alkalies, but if it be obtained by decomposing an alkaline tungstate with hydrochloric acid, it dissolves readily in solutions of the fixed alkalies and of ammonia.

Tungstic acid is capable of existing in several modifications, which bear to each other a relation similar to that between stannic and metastannic acids.²

Only the *tungstates of potassa, soda, and ammonia* are soluble in water. These salts are composed of single equivalents of acid and base.

The tungstates are decomposed by acids, being converted, first into acid tungstates, and ultimately into pure tungstic acid.

Solutions of the neutral tungstates of the alkalies are not precipitated by sulphuretted hydrogen, a soluble sulphur-salt being produced.

When tungstic acid, or a tungstate, is placed in contact with hydrochloric acid and zinc, the blue intermediate oxide of tungsten is obtained.

The tungstates of soda and lime have recently been applied in dyeing.

Tungstic acid combines with the strong mineral acids, forming sparingly-soluble compounds.

CHLORIDES OF TUNGSTEN.

The *bichloride* (WCl_2) is obtained by passing chlorine over tungsten heated in a tube; it forms small dark red needles, which are very fusible and volatile; it is decomposed by water.

The *trichloride* (WCl_3), also red, crystalline, and decomposed by water, is formed when sulphotungstic acid is heated in a current of chlorine. Its vapor has a red-brown color.

When chlorine is passed over tungstic acid, an oxychloride is obtained, of the formula WO_2Cl ; it forms yellow needles.

¹ Wright has obtained this compound by the action of other reducing agents upon bismuthate of soda; he assigns to it the formula $\text{WO}_2 \cdot \text{WO}_3 \cdot \text{NaO} \cdot \text{WO}_3$.

² Laurent, *Ann. Ch. Phys.* [3] xxi. 64.

SULPHIDES OF TUNGSTEN.

Tungstic acid, which has not been calcined, dissolves in the hydrosulphates of alkaline sulphides, forming sulphur-salts, from which acids precipitate the *tersulphide of tungsten*, or *sulphotungstic acid*, WS_3 ; this compound has a brown color, and loses sulphur when heated, leaving *black bisulphide of tungsten*.

Two *phosphides of tungsten* have recently been obtained by Wöhler. The compound W_2P_3 is a dark gray powder, prepared by heating tungsten in vapor of phosphorus. The other phosphide, W_4P_3 , is obtained in brilliant prisms, by reducing a mixture of tungstic and phosphoric acids, at a very high temperature, in a crucible lined with charcoal.

REACTIONS OF TUNGSTEN (*Tungstic acid*).—*Sulphuric, nitric, and hydrochloric acids*; white precipitate, insoluble in excess, but soluble in ammonia. These precipitates are soluble, to a slight extent, in water.

Hydrosulphuric acid; in neutral solutions, no precipitate, but if the solution be afterwards mixed with an acid, a brown precipitate is formed, which is soluble in sulphide of ammonium.

Reducing agents, such as *chloride of tin, zinc*, in presence of an acid, &c., produce a fine blue color.

With a bead of *phosphorous salt*; in the *outer flame*, a colorless or pale yellow glass, becoming blue in the inner flame. If iron be present, a blood-red bead is obtained in the inner flame, but the blue color is produced on the addition of a minute quantity of *metallic tin*.

MOLYBDENUM.

Sym. Mo. Eq. 46. Sp. Gr. 8.62.

§ 303. This metal is of rare occurrence in nature, in the form either of bisulphide (*molybdena*), or of molybdate of lead.

It may be obtained by heating molybdic acid to redness in a stream of hydrogen, or by exposing it, in a crucible lined with charcoal, to the strongest heat of a forge. The metal is obtained by the latter method, in masses having the appearance of dead silver, which acquire a lustre when rubbed. It is very infusible.

When exposed to air (especially if reduced by hydrogen), it is oxidized; if heated to redness in air, it is converted first into a brown oxide, then into a blue intermediate oxide, and lastly into white molybdic acid. Molybdenum decomposes steam at a high temperature.

Dilute sulphuric and hydrochloric acids do not attack it, but nitric acid oxidizes it rapidly, and converts it into molybdic acid; nitro-hydrochloric acid is the best solvent of molybdenum.

MOLYBDENUM AND OXYGEN.

(Prot-) oxide	MoO
Binoxide	MoO ₂
Molybdic acid	MoO ₃

OXIDE OF MOLYBDENUM, MoO.

Oxide or protoxide of molybdenum, may be prepared by dissolving a molybdate in an excess of hydrochloric acid, and introducing some metallic zinc; the

color passes, as the reduction proceeds, through different shades of blue and brown, and finally becomes black, when the solution contains chloride of molybdenum, from which the hydrated oxide is precipitated by adding an excess of potassa.

Hydrated oxide of molybdenum is brown, insoluble in the caustic alkalies, but soluble in carbonate of ammonia. It oxidizes rapidly when exposed to air.

This oxide dissolves in acids, forming salts.

When heated *in vacuo*, it loses water, and is afterwards converted, with sudden incandescence, into a modification which is insoluble in acids.

BINOXIDE OF MOLYBDENUM, MoO_2 .

This oxide is obtained in the anhydrous state by calcining molybdate of ammonia, or a mixture of molybdate of soda, with chloride of ammonium, with exclusion of air; it then forms a red-brown crystalline powder.

In order to obtain the hydrate, a solution of molybdic acid in hydrochloric acid is digested with copper, and the solution, then containing bichloride of molybdenum and chloride of copper, decomposed with excess of ammonia, which precipitates the hydrated binoxide of molybdenum.¹

This substance is very similar in appearance to hydrated sesquioxide of iron; it is oxidized by exposure to air. Bin oxide of molybdenum is a basic oxide.

MOLYBDIC ACID, MoO_3 .

This acid (which occurs native as *molybdic ochre*) is prepared by dissolving the native bisulphide of molybdenum in nitro-hydrochloric acid, evaporating to dryness, extracting the molybdic acid from the residue by treatment with ammonia, crystallising the molybdate of ammonia from the solution, and either separating the molybdic acid by hydrochloric acid, or by calcining the salt with access of air.

Molybdic acid (which has not been ignited) forms a white mass; it may be obtained in lustrous needles. When heated in close vessels, it fuses, and becomes yellow; if heated in a current of air, it sublimes easily, in a crystalline state. It is sparingly soluble in cold, but more soluble in hot water; the solution reddens litmus-paper. This acid expels carbonic acid from alkaline carbonates.

Reducing agents, as zinc, (proto-) sulphate of iron, &c., decompose molybdic acid, producing a blue intermediate oxide, the composition of which is expressed by the formula $\text{MoO}_3 \cdot 4\text{MoO}_2$. This compound is soluble in water, and is precipitated from the solution by chloride of ammonium. It is easily oxidized, even on exposure to air, and converted into molybdic acid. Acids dissolve it, forming blue solutions, which are decolorized by potassa.

A green intermediate oxide ($\text{MoO}_3 \cdot 2\text{MoO}_2$) is formed by the direct combination of its proximate constituents.

The *neutral molybdates* have the general formula $\text{MO} \cdot \text{MoO}_3$; the molybdates of the alkalies are colorless, crystallizable, and soluble.

The other molybdates are, for the most part, insoluble.

If the solution of a molybdate be not too dilute, the molybdic acid may be precipitated by stronger acids; the precipitate is soluble in excess of acid.

Molybdic acid exhibits a peculiar deportment towards phosphoric acid, which has been applied in testing for this latter. When a solution of molybdic acid is mixed with excess of ammonia, some phosphate of soda added, and afterwards an excess of nitric acid, a yellow precipitate is obtained, which was found by

¹ According to Kobell, a sesquioxide, and not a bin oxide, is obtained in this case; he doubts the existence of a bin oxide.

Sonnenschein to contain about 8 per cent. of phosphoric acid, and 86 per cent. of molybdic acid, together with molybdate of ammonia and water; the precipitate is insoluble in dilute acids, but soluble in alkalis and their carbonates. Arsenic acid does not yield a similar precipitate, unless the liquid be heated to boiling.

CHLORIDES OF MOLYBDENUM.

The (*proto-*) *chloride* is obtained by dissolving the hydrated (*prot-*) oxide in hydrochloric acid.

Bichloride of molybdenum, MoCl_6 , is obtained when molybdenum is heated in chlorine; it forms a red vapour, which condenses into crystals resembling iodine, and is easily soluble in water.

A soluble *oxy-chloride of molybdenum*, of the formula MoO_2Cl , has been prepared by heating binoxide of molybdenum in chlorine.

Bisulphide of molybdenum (MoS_2) is, as already mentioned, found native; it has a lead-gray color, and much resembles graphite; it is not affected by a moderate heat in closed vessels, but is converted into molybdic acid by roasting.

Nitric acid converts it into molybdic acid. Boiling concentrated sulphuric acid attacks it, producing a blue solution, and evolving sulphurous acid.

Two other sulphides of molybdenum exist, having the formulæ MoS_3 and MoS_4 .

REACTIONS OF MOLYBDENUM.—(*Protoxide.*)—*The alkalis*; a brownish-black precipitate, insoluble in excess.

The alkaline carbonates; brownish-black precipitates, slightly soluble in excess of the fixed alkaline carbonates, but more easily soluble in excess of carbonate of ammonia, from which solution the oxide is reprecipitated upon boiling.

Hydrosulphuric acid and *sulphide of ammonium* (the former not immediately); brown precipitates, soluble in sulphide of ammonium.

(*Binoxide.*)—*The alkalis*; dark-brown precipitates, insoluble in excess.

The alkaline carbonates; light-brown precipitates, soluble in excess.

Hydrosulphuric acid and *sulphide of ammonium* (the former after a time); brown precipitates, soluble in sulphide of ammonium.

Ferrocyanide and *ferricyanide of potassium*; brown precipitates.

(*Molybdic acid.*)—*Hydrochloric* and *nitric acids*; in moderately concentrated solutions, white precipitates, soluble in excess.

Hydrosulphuric acid; in acid solutions, a brown precipitate, the supernatant liquid being green. If the solution is dilute, a green color only is obtained. The addition of a very small quantity of sulphuretted hydrogen colors the solution blue.

Sulphide of ammonium, after some time, renders solutions of alkaline molybdates of a golden-yellow color, and acids precipitate brown tersulphide of molybdenum.

Chloride of tin; a greenish-blue precipitate, or, in dilute solutions, a blue coloration.

Tin, zinc, and copper; in acid solutions, a blue coloration, afterwards becoming green, and finally brown.

With a bead of *microcosmic salt*; in the inner blowpipe-flame, a green bead, the color of which is fainter in the outer flame; with *borax* in the inner flame, a brownish-red bead.

TELLURIUM.

Sym. Te. Eq. 64.2. Sp. Gr. 6.2.

§ 304. This very rare element presents so great an analogy to sulphur and selenium that it is often classed among the non-metallic bodies.

Tellurium was originally discovered in certain Transylvanian gold ores, in combination with gold, silver, copper, and lead; it has been more recently found in combination with bismuth.

Preparation.—The telluride of bismuth is heated to bright redness, with an equal weight of carbonate of potassa and charcoal; the bismuth is reduced, while the tellurium is converted into telluride of potassium, which dissolves when the fused mass is treated with water; when this (purplish-red) solution is exposed to air, the tellurium is deposited, and may be purified by washing with a little acid.

Properties.—Tellurium has a silvery lustre; in texture it is crystalline and brittle. It fuses at about the same temperature as antimony, crystallizes easily from a fused state, and appears to be isomorphous with antimony and arsenic. Tellurium volatilizes at a high temperature. When heated in air, it burns with a bright-blue flame.

It dissolves unchanged in concentrated sulphuric acid, imparting to it a purple-red color. When heated with solutions of the alkalies, it yields tellurides and tellurites.

TELLURIUM AND OXYGEN.

Tellurous acid	TeO_2 .
Telluric acid	TeO_3 .

TELLUROUS ACID, TeO_2 .

This acid is obtained when tellurium is burnt with free access of air. It may be prepared by oxidizing the metal with nitric acid, or by decomposing bichloride of tellurium with water, when the acid is deposited in octohedra.

Tellurous acid is a white, crystalline, fusible powder, capable of sublimation, and insoluble in water and acids; it dissolves in alkalies, forming tellurites, from which acids precipitate the hydrated tellurous acid; this hydrate is soluble in hydrochloric acid, and expels the carbonic acid when heated with solutions of alkaline carbonates.

TELLURIC ACID, TeO_3 .

Telluric acid is prepared by passing chlorine, to saturation, into a solution of tellurite of potassa, mixed with excess of potassa; the solution of tellurate of potassa thus obtained is precipitated by chloride of barium, and the tellurate of baryta decomposed with sulphuric acid.

The hydrated telluric acid crystallizes in six-sided prisms, containing three eqs. of water, and is soluble; when moderately heated it loses two eqs. of water, and at a higher temperature, becomes anhydrous and insoluble; if heated still further, it loses oxygen, and is converted into tellurous acid.

If a solution of a tellurate be acidulated with hydrochloric acid, and heated with sulphurous acid, a black precipitate of tellurium is formed.

The tellurates evolve oxygen when heated, leaving tellurites. They are decomposed even by acetic acid.

TELLURETTED HYDROGEN. HYDROTELLURIC ACID, HTe.

This compound is obtained by decomposing telluride of potassium or of iron with hydrochloric acid.

It is a colorless gas, having an odor like that of sulphuretted hydrogen; its specific gravity is 5.12.

Telluretted hydrogen is soluble in water; the solution is decomposed by the oxygen of the air, and yields a brown precipitate of tellurium. It is inflammable, and deposits tellurium when burnt. It acts upon solutions of metallic oxides like hydrosulphuric acid.

CHLORIDE OF TELLURIUM (TeCl) obtained by strongly heating the metal in a feeble current of chlorine, is a black solid; its vapor is violet-colored.

Water decomposes the chloride into bichloride and metal.

The *bichloride* (TeCl_2) is prepared by gently heating tellurium in an excess of chlorine; it is a white, crystalline, volatile solid, soluble in water.

A *bisulphide* and a *tersulphide of tellurium* are known; the latter is very unstable. These sulphides are sulphur-acids.

The tellurides of the metals are very similar to the sulphides and selenides. The alkaline tellurides have a reddish-brown color, and yield red solutions. When a telluride is boiled with nitric acid, tellurous acid is formed, the other metal being converted into a nitrate.

REACTIONS OF TELLURIUM (*Tellurous acid*).—Alkalies and their carbonates; white precipitate, soluble in excess.

Hydrosulphuric acid, in acid solutions, brown precipitate, soluble in the alkaline sulphides.

Reducing agents, *e. g.* *sulphurous acid, chloride of tin, zinc, &c.*; black precipitate.

(*Telluric Acid*).—*Hydrosulphuric acid*, in acid solutions, black precipitate, soluble in alkaline sulphides.

Reducing agents; same result as with tellurous acid.

TITANIUM.

(Although the reactions of this metal would entitle it to a place in the third group, it so much resembles tin, in the general characters of its compounds, that we have deferred giving its history until that metal had been described.)

Sym. Ti. Eq. 25. Sp. Gr. 5.3.

§ 305. Titanium is a rare metal, which, in its compounds, very much resembles tin.

It is found in nature chiefly in the minerals rutile, anatase, brookite, and titanite iron.

Rutile, brookite, and anatase, are almost entirely composed of titanite acid.

Titanite iron ores contain titanate of iron mixed with more or less oxide of iron.

Titanite, or *spinel*, is a compound of titanate and silicate of lime.

Preparation.—The following process is that generally adopted for the preparation of titanium.

A mixture of finely-powdered rutile with twice its weight of carbonate of potassium is fused in a platinum crucible; the fused mass is powdered, and treated with dilute hydrosulphuric acid, which converts it into a sparingly-soluble titanate of potassium, a double fluoride of titanium and potassium). This compound is ignited to expel all traces of water, and heated in a covered platinum

crucible with potassium; when the violent reaction has terminated, the mass is allowed to cool and treated with water, which dissolves the fluoride of potassium, leaving only the titanium.

Properties.—Titanium thus obtained is a dark green, infusible, amorphous powder. When heated in air, it burns vividly, and is converted into titanous acid. When heated with oxide of lead or of copper, it is also converted into titanous acid with vivid incandescence.

Titanium decomposes water even at the boiling-point, producing titanous acid.

This metal is dissolved by hot hydrochloric acid, with disengagement of hydrogen.¹ When fused with a mixture of hydrate and nitrate of potassa, it is converted into titanate of potassa.

TITANIUM AND OXYGEN.

Oxide of titanium	TiO
Sesquioxide "	Ti ₂ O ₃
Titanic acid	TiO ₂

OXIDE, OR PROTOXIDE OF TITANIUM, TiO.

This oxide is obtained when titanous acid is heated with potassium. It has a black color, and is infusible; when heated in air, it is converted into titanous acid. Oxide of titanium dissolves slowly in acids and alkalies; it forms a blue hydrate, which absorbs oxygen from the air, and decomposes water.

SESQUIOXIDE OF TITANIUM, Ti₂O₃.

When titanous acid is reduced by hydrogen at a high temperature, the sesquioxide is obtained as a black powder. The hydrate falls as a gelatinous brown precipitate when sesquichloride of titanium is decomposed by alkalies; when exposed to air, it absorbs oxygen, becoming black, then blue, and lastly white, being converted into titanous acid.

Sesquioxide of titanium possesses basic characters; it dissolves in sulphuric acid, forming a violet solution.

TITANIC ACID, TiO₂.

Titanic acid, as before mentioned, is found nearly pure in rutile, which contains generally 1 or 2 per cent. of oxide of iron.

Rutile is isomorphous with native binocide of tin, and, like that mineral, is not attacked by acids.

Anatase, also nearly pure titanous acid, forms fine blue crystals.

Brookite forms opaque prismatic crystals, and contains very little iron.

Preparation.—In order to obtain perfectly pure titanous acid, finely-powdered rutile is fused, at a very high temperature, with 2 or 3 times its weight of chloride of barium. The fused mass is powdered and treated with hot water, which dissolves the excess of chloride of barium, leaving a residue of titanate of baryta and sesquioxide of iron; this residue is boiled with concentrated sulphuric acid, the greater excess of the latter expelled by heat, and the residue treated with water; the whole of the baryta is left as insoluble sulphate, whilst the solution contains the titanous acid in combination with sulphuric acid, together with sulphate of sesquioxide of iron; a little sulphuretted hydrogen is passed through the solution, to remove any tin which might be present, and the acid is then neutralised with ammonia, which precipitates the titanous acid colored with a little

¹ Wöhler.

sulphide of iron; the supernatant liquor is decanted from the precipitate, and the latter digested with a solution of sulphurous acid, which removes the sulphide of iron in the form of hyposulphite, and leaves the titanous acid in a state of purity.

Properties.—The hydrate ($\text{TiO}_2 \cdot \text{HO}$) in appearance much resembles alumina; it is distinguished by a remarkable tendency to pass through filters; it is soluble in some acids (e. g. hydrochloric), but not readily in alkalis.

The acid solutions deposit most of the titanous acid when boiled. When dried, hydrated titanous acid becomes insoluble in all acids except concentrated sulphuric; it assumes a yellow color when heated, and becomes white again on cooling.

Anhydrous titanous acid is infusible, fixed, and insoluble; it reddens blue litmus. When titanous acid is fused with alkalis, it forms masses which crystallize on cooling, and are decomposed by water into insoluble and highly acid titanates, whilst but little titanous acid is found in solution.

NITRIDES OF TITANIUM.—When bichloride of titanium is treated with dry ammonia, it forms a white compound, which, when heated in a stream of ammoniacal gas, leaves a residue of brilliant purple scales of nitride of titanium, having the formula Ti_2N_3 . When this compound is heated in a current of hydrogen, yellow lustrous scales are obtained, the composition of which is Ti_2N_3 .

If titanous acid be heated in a porcelain tube through which dry ammonia is passed, it is converted into a violet powder, which is a third nitride of titanium, TiN .

In the furnaces in which iron-ores containing titanium are smelted, crystals are sometimes found, which were formerly thought to be metallic titanium, but have been recently shown to be represented by the formula Ti_{32}N_8 . This most curious compound forms coppery-red cubical crystals, which volatilize at a high temperature, and are so hard as to scratch quartz.

The nitrides of titanium are remarkable for their stability, resisting a high temperature without decomposition.

CHLORIDES OF TITANIUM.

Sequichloride of Titanium, Ti_2Cl_6 , is obtained by passing through a tube heated to redness, a current of hydrogen saturated at 212°F . (100°C .) with vapor of bichloride of titanium, when crystals of the sequichloride condense upon the cooler parts of the tube:—



This compound forms dark violet scales, which deliquesce when exposed to air, forming a violet liquid. It is a most powerful dechlorinating (or deoxidizing) agent; it precipitates the noble metals from their solutions, reduces the higher oxides of iron and copper, and is even said to be capable of separating sulphur from sulphurous acid.

Bichloride of Titanium, TiCl_4 , is prepared by passing chlorine over a mixture of titanous acid and carbon at a red heat. It forms a colorless liquid, very similar to bichloride of tin; it fumes in the air, and boils at 275°F . (135°C .) In its behavior with water it much resembles the bichloride of tin; with a small quantity it combines, forming a crystalline compound, which is decomposed by a larger quantity into hydrochloric acid and titanous acid; this latter is partly dissolved by the hydrochloric acid, but is reprecipitated on boiling.

Bisulphide of Titanium (TiS_2) is formed by passing through a tube heated to redness, a mixture of sulphuretted hydrogen and vapor of bichloride of titanium.

It forms brilliant yellow scales, very similar to *aurum musivum* (bisulphide of tin), which are decomposed by moist air, evolving sulphuretted hydrogen; when heated in air, bisulphide of titanium is converted into sulphurous and

titanic acids; hydrochloric acid decomposes it with disengagement of hydro-sulphuric acid.

REACTIONS OF TITANIUM (*Sesquioxide*).—*Alkalies and their carbonates*; dark brown precipitates gradually decomposing water, becoming black, blue, and finally white.

Sulphide of ammonium, a similar precipitate.

Solutions of gold, silver, and mercury are reduced to the metallic state.

(*Titanic Acid*).—*Alkalies and alkaline carbonates*; white precipitate, insoluble in excess.

Sulphide of ammonium; a similar precipitate.

Oxalic acid; white precipitate (if the solution do not contain too much hydrochloric acid).

Metallic zinc; in presence of free acid, a blue solution which deposits, after a time, a blue precipitate, becoming white on standing.

With a bead of *phosphorus-salt*, in the inner flame, a bead which is yellow while hot, and becomes violet on cooling; in the outer flame the bead is rendered colorless. If iron be present, the bead produced in the inner flame assumes a brown-red color on cooling; the blue color may then be produced by an addition of *tia*.

METALS OF THE FIFTH GROUP.

MERCURY.¹

(*Quicksilver.*)

Sym. Hg. Eq. 100. Sp. Gr. 13.595.

§ 306. THIS is the only metal which is not solid at ordinary temperatures.

The mercury of commerce is never perfectly pure, as may be seen by scattering a little upon a smooth plate of glass, when, instead of forming small spheroidal globules, as is the case with the pure metal, it gives pyriform drops which leave a gray trace where they roll along the glass.

When mercury is very impure, it is subjected to distillation, the iron bottles in which it is imported being used as retorts; but since this process is very rarely executed in laboratories, we shall not enter into details respecting it.

The simplest process for purifying mercury from the lead and tin which the commercial metal usually contains, consists in stirring it in a Wedgwood or porcelain dish, with a mixture of nitric acid and two volumes of water; the contents of the dish are heated to about 130° F. (54° 5 C.) for several hours, with frequent agitation; the foreign metals, being more easily oxidized than the mercury, are dissolved by the acid, while that metal is left in a state of purity; the supernatant liquid is removed by decantation, the mercury well washed with water, and dried, first with blotting-paper, and afterwards by a gentle heat. Should it be found that the mercury is still impure, the treatment with nitric acid may be repeated.

Properties.—Pure mercury has a slightly bluish-white color and a brilliant lustre. It solidifies at a temperature of -40° F. (-40° C.), which may be obtained with solid carbonic acid and ether, or more easily with pounded ice and crystallized chloride of calcium. If it be slowly solidified, the metal crystallizes in octohedra. Solid mercury much resembles lead and tin in malleability and tenacity; its specific gravity is 13.59, showing that, like water, mercury expands in the act of solidifying.

This metal boils at about 660° F. (349° C.) yielding a transparent vapor of sp. gr. 6.976.

Mercury suffers a very considerable expansion by heat; and since, between the

¹ Mercury and lead, although often occurring, in the course of analysis, under the fourth group, are here placed by the side of silver, because mercury forms a subchloride which, like chloride of silver, is insoluble in water; and the chloride of lead, though not absolutely insoluble, is most frequently precipitated together with the chloride of silver and subchloride of mercury. We seize this opportunity of repeating the caution given in the outset, that this classification should only be regarded as an arbitrary division, intended to facilitate the subsequent study of analysis, and not as founded upon any close analogies in the chemical relations of the metals composing individual groups. The other methods of arranging the metals (according to their affinity for oxygen, or their power of decomposing water), although more strictly philosophical, have appeared to us to possess less practical utility than the division which we have adopted.

freezing and boiling-points of water, its expansion is nearly proportional to the amount of heat which it receives, it is very useful for thermometric purposes. The expansion suffered by this metal between 32° F. and 212° F. amounts to 0.018153 of its volume at 32°.

That mercury volatilizes even at ordinary temperatures, is shown by the condensation of minute globules of the metal in the vacuum of the barometer. It appears, however, that the properties of vapor of mercury differ from those of ordinary vapors, for it is found that if a leaf of gold be suspended in a bottle containing a small quantity of mercury at a rather low temperature, only that portion of the gold which is nearest to the mercury becomes whitened, the upper part retaining its yellow color, showing that the atmosphere of mercurial vapor is limited to a small space above the surface of the metal.¹

When mercury is boiled with water, a considerable quantity of the metal passes over with the steam.

Perfectly pure mercury evinces no attraction for surfaces of glass or porcelain, so that in vessels made of these materials, the mercury assumes a convex surface; but if $\frac{1}{1000}$ of lead be dissolved in it, the surface is plane: this circumstance is turned to advantage in the graduation of glass tubes with the aid of mercury.

When mercury is violently agitated with saline solutions, it is divided into numerous minute globules, which are reunited with some difficulty. Mercury is capable of retaining, mechanically, small quantities of air and water, from which it can be freed only by continued ebullition.

This metal is not, to any extent, and it is questionable whether it be in the least, affected by exposure to air at the ordinary temperature; when heated to a temperature approaching its boiling-point, for some hours, in a long-necked flask, with free access of air, it is, to a considerable extent, converted into small red crystals of oxide of mercury. This experiment must always possess a peculiar interest, since, in the hands of Lavoisier, it gave rise to the discovery of the composition of atmospheric air.

Mercury does not decompose water at any temperature.

Nitric acid dissolves mercury even at the ordinary temperature, but very rapidly when heated, producing nitrate of the suboxide, or of the oxide, according as the metal or the acid is in excess.

Hydrochloric acid does not act upon mercury; hydriodic and hydrosulphuric acids convert it, respectively, into subiodide and subsulphide of mercury, hydrogen being set free.

Dilute sulphuric acid has no action upon mercury, but the concentrated acid, with the aid of heat, converts it into a sulphate of one of its oxides, sulphurous acid being disengaged. Mercury combines directly with chlorine, bromine, iodine, sulphur, and with many of the metals, especially with potassium, sodium, zinc, copper, gold, tin, and lead. Its compounds with the metals are termed amalgams.

Mercury exerts a powerful action upon the animal economy, and materially injures the health of workmen engaged in employments where this metal is largely used.

MERCURY AND OXYGEN.

Suboxide	Hg ₂ O
Oxide ^a	HgO

¹ Karsten has found that the volatilization of mercury is perceptible even at temperatures below 32°.

^a The equivalent of mercury was formerly considered by some chemists as 200, when the suboxide of mercury was regarded as a protoxide, HgO, and the present protoxide was looked upon as a binoxide, HgO₂.

SUBOXIDE OF MERCURY, BLACK OXIDE, Hg_2O .

§ 307. *Preparation*.—The black oxide may be prepared by decomposing precipitated subchloride of mercury with cold potassa, light being excluded. It is also obtained as a black precipitate when a solution of a salt of suboxide of mercury is decomposed by potassa, but is then almost always mixed with metallic mercury (arising from the decomposition of a part of the suboxide), as may be seen by examining the precipitate with a lens, or by triturating it in a mortar, when the metal accumulates into globules.

Properties.—Suboxide of mercury is a weak base; it has a black color and is exceedingly unstable, being decomposed by exposure to light, or to a slightly elevated temperature, into oxide of mercury and free metal:—



this speaks strongly in favor of its being a suboxide.

The soluble neutral salts of suboxide of mercury have an acid reaction.

NITRATE OF SUBOXIDE OF MERCURY, SUBNITRATE OF MERCURY,
PROTONITRATE OF MERCURY, $Hg_2O.NO_3$.

This salt is prepared by acting upon a slight excess of mercury with nitric acid, in the cold; it is also formed when peroxide of nitrogen (NO_2) acts upon metallic mercury.

This nitrate forms fine colorless crystals of the formula $Hg_2O.NO_3 + 2Aq$, which dissolve in nitric acid, but are decomposed by water into a *basic nitrate*, $2Hg_2O.NO_3$, which is precipitated, and an acid nitrate which passes into solution.

The same basic nitrate is deposited in oblique rhombic prisms of the formula $2Hg_2O.NO_3 + HO$, when the neutral nitrate is dissolved in a small quantity of hot water or nitric acid, and the solution allowed to cool. When the neutral nitrate is heated, a yellow basic compound is produced, the composition of which is expressed by the formula $Hg_2O.2Hg_2O.NO_3$.

When a very large excess of mercury is acted on by nitric acid in the cold, crystals of a *basic nitrate* are deposited, having the composition $3Hg_2O.2NO_3 + 3Aq$. This salt may readily be distinguished from the neutral salt by triturating in a mortar with a little chloride of sodium; the neutral salt remains white, but the basic compound gives a black color, from the separation of suboxide of mercury.

The compound known as *hydrargyri precipitatum nigrum*, or *Hannemann's soluble mercury*, is prepared by adding very dilute ammonia to a solution of the nitrate of suboxide of mercury in dilute nitric acid, as long as a gray precipitate is formed. This gray precipitate, which is the compound in question, varies in composition, but is generally considered as a combination of ammonia with a basic nitrate of suboxide of mercury, $2Hg_2O.NO_3.NH_3$.

SULPHATE OF SUBOXIDE OF MERCURY, SUBSULPHATE OF MERCURY.



When dilute sulphuric acid is added to a solution of nitrate of suboxide of mercury, this sulphate is precipitated as a white crystalline powder. It may also be obtained by gently heating an excess of mercury with concentrated sulphuric acid.

Sulphate of suboxide of mercury is very sparingly soluble in water; it crystallizes in prisms; a small quantity of alkali decomposes it, producing an insoluble basic salt.

The *chromate of suboxide of mercury* ($Hg_2O.CrO_3$) is precipitated when chro-

mate of potassa is added to nitrate of suboxide of mercury. It has an orange-red color, and leaves a residue of pure sesquioxide of chromium when ignited.

OXIDE, OR PROTOXIDE, OF MERCURY, RED OXIDE.

HgO. Eq. 108.

§ 308. *Preparation.*—I. This oxide is formed, as already mentioned, when mercury is heated for some time, near its boiling-point, in contact with air; the minute crystalline scales thus formed, were termed by the old chemists *precipitatum per se*.

II. The red oxide of mercury is generally obtained by calcining the nitrate at a moderate heat; it is then commonly called *nitric oxide of mercury*.

The external appearance of the oxide thus obtained depends upon that of the nitrate. Nitrate of mercury in powder yields a pulverulent oxide of an orange yellow color; when the nitrate is in crystals, a crystalline oxide is obtained; the red crystalline oxide of commerce is prepared by heating minute crystals of nitrate of mercury.

III. When an excess of potassa is added to a solution of chloride of mercury (corrosive sublimate), a yellow amorphous precipitate of oxide of mercury is obtained; this should be collected upon a filter, and well washed with boiling water till the washings leave no residue on evaporation.

Properties.—We have seen that oxide of mercury is capable of existing in two states, in one of which it is yellow, in the other, red; these manifest, also, some difference in their chemical properties; thus, the yellow modification combines with oxalic acid in the cold, which is not the case with the red variety; again, an alcoholic solution of corrosive sublimate converts the yellow oxide into a black oxychloride, while the red oxide is not affected by it.

Oxide of mercury is slightly blackened by exposure to light, being decomposed to some extent. When heated, oxide of mercury assumes a dark brown, nearly black color, but regains its original color on cooling; a heat somewhat below redness resolves it into its elements.

Oxide of mercury is slightly soluble in water, the solution has an alkaline reaction to very delicate color-tests; it combines readily with most acids, forming definite salts. The soluble neutral salts redden litmus. It is a powerful oxidizing agent, and is often employed as such in the laboratory; it will be remembered that oxide of mercury is employed to convert chlorine into hypochlorous acid. It is also used to complete the incineration of organic substances, and to reconvert any sulphides, produced in the process of incineration, into sulphates.

OXY-AMIDIDE OF MERCURY, AMMONIATED OXIDE OF MERCURY.

$3\text{HgO} \cdot \text{HgNH}_2$.

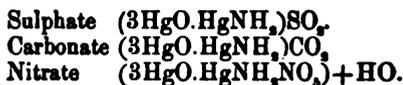
When oxide of mercury (especially the yellow modification) is treated with ammonia, a compound is produced, which is represented by some chemists as an ammoniated oxide of mercury, $4\text{HgO} \cdot \text{NH}_3 \cdot 2\text{HO}$, and by others as a hydrated oxy-amidide of mercury, $3\text{HgO} \cdot \text{HgNH}_2 + 3\text{HO}$. This latter view seems to account more satisfactorily for the various changes which this substance undergoes.

This base has a yellow color, and is decomposed by exposure to light; it decrepitates when rubbed in a mortar. When exposed for a long time *in vacuo* over quicklime, or when heated to 266°F . (130°C .), it loses its water, becoming $3\text{HgO} \cdot \text{HgNH}_2$, which has a brown color.

It is insoluble in water and alcohol. The hydrated oxy-amidide of mercury is not decomposed by solution of potassa in the cold, but, when heated with it, disengages ammonia; the anhydrous compound only disengages ammonia when fused with hydrate of potassa.

The basic characters of the oxy-amidide of mercury are very well marked; it absorbs carbonic acid from the air, and disengages ammonia from ammoniacal salts.

It combines readily with oxygen-acids; the following are examples of the salts thus formed:—



When treated with hydrogen acids, it gives rise to water and to salts of the radicals of these acids.

Two chlorides exist, having, respectively, the formulæ 2HgO.HgCl.HgNH_2 and 3HgCl.HgNH_2 ; the iodide corresponds to the former of these chlorides.

NITRATE OF OXIDE OF MERCURY, HgO.NO_2 .

This salt may be prepared by dissolving mercury or oxide of mercury in excess of nitric acid, with the aid of heat; if an attempt be made to crystallize the salt in the ordinary way from this solution, a basic salt will be obtained, but by dissolving oxide of mercury in excess of nitric acid, so as to obtain a syrupy liquid, and exposing this to a refrigerating mixture, crystals may be obtained, of the formula $\text{HgO.NO}_2.2\text{HO}$.

If the solution of this nitrate be evaporated, crystals are deposited, of the formula $2\text{HgONO}_2+2\text{HO}$; this *basic salt* may also be obtained by digesting the solution of the neutral nitrate with an excess of recently precipitated oxide of mercury.

These salts are decomposed by water, yielding a basic nitrate having the composition $3\text{HgO.NO}_2.\text{HO}$; by continued washing with boiling water, this basic salt is converted into the red oxide of mercury. The basic salt is remarkable for its difficult solubility in nitric and sulphuric acids.

When solution of nitrate of oxide of mercury is digested with metallic mercury, the latter is gradually dissolved, nitrate of suboxide of mercury being produced.

By adding ammonia to a solution of nitrate of oxide of mercury, a white precipitate is obtained which appears to be the nitrate of the oxy-amidide of mercury mentioned above.

SULPHATE OF OXIDE OF MERCURY, HgO.SO_4 .

The sulphate is obtained, as a white crystalline powder, by boiling mercury with an excess of concentrated sulphuric acid, until the latter begins to pass off in vapor; on the large scale, the boiling is carried to dryness, in order to expel excess of acid.

Sulphate of oxide of mercury crystallizes in white deliquescent needles; when treated with cold water it is decomposed, a yellow basic salt being produced, which is known as *turbith mineral*, and a highly acid salt being dissolved. The formula of turbith mineral is 3HgO.SO_4 ; it is converted into oxide of mercury by long boiling with water.

Sulphate of oxide of mercury is employed for the preparation of corrosive sublimate.

When sulphate of oxide of mercury is treated with an excess of ammonia, it produces the sulphate of oxy-amidide of mercury.

Sulphate of mercury is capable of forming crystalline compounds by direct combination with different proportions of ammonia.

Two *basic carbonates of oxide of mercury* having the formulæ, respectively, 4HgO.CO_2 and 3HgO.CO_2 , are obtained as red-brown precipitates by adding a

solution of nitrate of oxide of mercury to solutions of carbonate and bicarbonate of potassa employed in excess.

NITRIDE OF MERCURY, Hg_2N .

§ 309. This compound has been obtained by passing a stream of ammoniacal gas over precipitated red oxide of mercury, as long as the ammonia is absorbed, and afterwards heating the compound in an oil-bath to 266° F. (130° C.), whilst the stream of ammonia is still maintained, until no more water is formed:—



The product is washed with a little very dilute nitric acid to remove the excess of oxide of mercury.

Nitride of mercury is a dark-brown powder, which detonates when heated; it is insoluble in water, and dissolves slowly in the dilute acids, producing salts of ammonia and of oxide of mercury; it is so unstable that it detonates even when struck.

SUBCHLORIDE OF MERCURY, CALOMEL, Hg_2Cl .

Preparation.—The simplest method of preparing the subchloride of mercury, consists in decomposing a solution of subnitrate of mercury with chloride of sodium, when a slightly yellowish-white precipitate is formed, which must be collected upon a filter and well washed:—



It may also be prepared by intimately mixing the chloride of mercury (corrosive sublimate) with 1 eq. of metallic mercury, with addition of a little water, drying the mixture thoroughly, and subliming it:—



A more convenient method is to sublime a mixture of sulphate of suboxide of mercury and chloride of sodium:—



Since, however, it is very difficult to obtain the sulphate of suboxide of mercury in a state of perfect purity, it is customary to replace it by a mixture of sulphate of the oxide with 1 eq. of metallic mercury.

The following is the prescription of the London Pharmacopœia for the preparation of calomel:—

2 parts of mercury are dissolved, with the aid of heat, in 3 parts of concentrated sulphuric acid, and the solution evaporated to dryness:—



The residue of sulphate of oxide of mercury is intimately mixed with 2 more parts of mercury, and the mixture afterwards triturated with 1½ parts of chloride of sodium until globules are no longer visible; the whole is then sublimed in an appropriate vessel; the production of the subchloride of mercury is thus represented:—



The calomel thus prepared, however, is always more or less contaminated with corrosive sublimate, which, being exceedingly poisonous, must always be entirely removed from the calomel before its employment medicinally; the removal of the corrosive sublimate is effected by washing the calomel with water until the washings are no longer tinged by sulphuretted hydrogen.

For medicinal purposes, the calomel is obtained in a very finely divided state, by subliming it into chambers sufficiently large to allow it to condense before coming in contact with the walls.

Pure calomel should leave no residue when heated on platinum; when agitated with hot water, and filtered, the solution should give no precipitate or coloration with sulphuretted hydrogen or solution of potassa.

Properties.—Subchloride of mercury is not absolutely white; in large masses it has a yellow tint. It may be crystallized, by careful sublimation, in four-sided prisms with tetrahedral summits. It is slowly decomposed by exposure to light, into mercury and chloride of mercury, assuming a gray color. It is readily converted into vapor by a moderate heat, and fuses at or near its point of volatilization.

Subchloride of mercury is almost totally insoluble in water; concentrated nitric acid, with the aid of heat, dissolves it, producing chloride of mercury, and nitrate of the oxide. When boiled with hydrochloric acid, it is decomposed into chloride of mercury and metal, which separates. The alkalis convert it into black suboxide of mercury. Alkaline chlorides, especially in presence of organic matters, are said to be capable of decomposing it into metallic mercury and chloride of mercury, which would help to throw some light upon its therapeutic action.

Calomel dissolves in solution of chlorine, being converted into corrosive sublimate.

Ammoniacal gas is absorbed by subchloride of mercury, a compound being produced, of the formula $Hg_2Cl_2NH_3$.

When calomel is treated with liquefied ammonia, a gray compound is produced, having the composition $Hg_2Cl_2.HgNH_2$, which is therefore a double compound of amide and subchloride of mercury.

CHLORIDE OF PROTOCHLORIDE OF MERCURY, CORROSIVE SUBLIMATE.

HgCl.

§ 310. *Preparation.*—The chloride of mercury may be prepared by dissolving mercury in nitro-hydrochloric acid, and evaporating the solution to crystallization. It is, however, obtained on the large scale by heating a mixture of sulphate of oxide of mercury and chloride of sodium:—



2 parts of mercury are dissolved in 3 parts of sulphuric acid, with the aid of heat, the solution evaporated to dryness, and the residue mixed with $1\frac{1}{2}$ parts of chloride of sodium.

Since the sulphate of oxide of mercury often contains sulphate of the suboxide, some calomel might be produced in the above process; to avoid this, $\frac{1}{2}$ part of binoxide of manganese is often added to the above ingredients.

The mixture is introduced into a large glass flask, which is then imbedded in sand up to the neck; the sand-bath is furnished with a hood to carry off the mercurial vapors which may escape; a gradual heat is applied at first to expel all moisture; the sand is then removed so as to leave the upper part of the flask uncovered, and the heat increased; the chloride of mercury sublimes, and condenses on the cool part of the flask; when the sublimation has been continued for 8 or 10 hours, the heat is considerably increased in order to fuse the chloride partially, thus rendering it more compact; the flasks, when cold, are broken up, and the sublimate removed.

Properties.—Corrosive sublimate occurs in commerce in the form of transparent colorless masses, possessing considerable lustre, and bearing evidence of a crystalline texture; the density of this substance is 6.5. It fuses at about 509° F. (265° C.), and boils at 563° F. (295° C.), yielding a colorless vapor, which condenses in colorless octohedra upon a cold surface.

Corrosive sublimate dissolves in 16 parts of boiling and in 3 parts of cold water; its aqueous solution has an acid reaction, and when exposed to light,

becomes more strongly acid, and deposits a white precipitate of subchloride of mercury. It is much more soluble in alcohol and ether than in water; 1 part of chloride of mercury dissolves in 2½ parts of cold alcohol, and in 1½ of boiling alcohol; 3 parts of cold ether also dissolve 1 part of this substance. If an aqueous solution of corrosive sublimate be agitated with ether, the latter removes the greater part of the salt, which may be obtained by evaporation.

Chloride of mercury crystallizes from its solutions in a right rhombic prism, or some form derived from it.

Hydrochloric and nitric acids readily dissolve chloride of mercury, without alteration.

The fixed alkalis and their carbonates, when not added in excess to a solution of corrosive sublimate, give red-brown precipitates, which are oxychlorides of mercury.

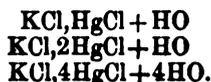
Ammonia produces, in solution of chloride of mercury, a white precipitate, to which we shall recur presently.

We have seen that when triturated with metallic mercury, the chloride passes into subchloride.

Corrosive sublimate is entirely precipitated from its solutions by albumen, which forms with it a perfectly insoluble compound; hence the use of the white of egg as an antidote in cases of poisoning by corrosive sublimate. This property of forming insoluble compounds with albumen and organic substances of a similar nature, may perhaps explain the powerful antiseptic qualities of corrosive sublimate, which lead to its employment for the preservation of wood, of anatomical preparations, &c.

Chloride of mercury forms a great many crystallizable double-salts with other metallic chlorides.

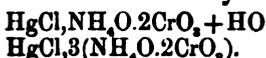
Three double chlorides of potassium and mercury are known to exist; their formulæ are the following:—



The double chloride of ammonium and mercury has the composition



Chloride of mercury combines with the bichromates of potassa and ammonia, forming crystallizable double compounds. The double compound with bichromate of potassa has, according to Millon, the formula, HgCl, KO.2CrO_3 , whilst those with bichromate of ammonia were found by Richmond and J. Abel to be



Uses.—Chloride of mercury is frequently used in the laboratory, either as a reagent, or in order to obtain some of the volatile metallic chlorides; thus, it will be recollected that bichloride of tin is prepared by distilling a mixture of metallic tin with corrosive sublimate.

The employment of this substance for preserving wood and anatomical preparations has been mentioned above; the preservative liquid known as *Goadby's solution* is composed as follows:—

Bay salt	4 oz.
Alum	2 oz.
Corrosive sublimate	2 grs.
Water	2 pts.

This solution is, however, somewhat objectionable for the preservation of substances actually under dissection, since the knives are much corroded both by the alum and by the mercury-salt.

OXYCHLORIDES OF MERCURY.

When chlorine is allowed to act upon an excess of oxide of mercury (as in the preparation of hypochlorous acid, see p. 137), an insoluble substance is produced, varying in color from brick-red to black, which is composed of one or more oxychlorides of mercury.

Three such compounds may be prepared, either by the above method, or by boiling solution of corrosive sublimate with oxide of mercury, or lastly, by decomposing the solution of corrosive sublimate with alkalies or alkaline carbonates in different proportions, but always in too small quantity to decompose the whole of the chloride. These oxychlorides are insoluble in water.

A white, somewhat soluble oxychloride, of the formula 2HgCl.HgO , always accompanies the oxychloride obtained by the action of chloride of mercury upon the oxide at high temperatures; the formula of this compound is HgCl.2HgO ; it may be either amorphous or crystalline, red, purple, or black; if black, it yields the red oxide of mercury when decomposed by alkalies, but in the other states, it gives the yellow oxide.

The oxychloride of the formula HgCl.3HgO may be also amorphous or crystalline, and varies in color from brownish-yellow to dark brown; it always yields the yellow oxide of mercury.

HgCl.4HgO resembles the preceding, but always yields the red oxide when decomposed.

A compound of the formula HgCl.6HgO has also been obtained.

AMIDO-CHLORIDE (OR CHLORAMIDIDE) OF MERCURY.

WHITE PRECIPITATE. HgCl.HgNH_2 ,¹

This compound is prepared by decomposing solution of corrosive sublimate with an excess of ammonia:—



It is a fine white amorphous powder; when heated to about 680° F. (360° C.) it evolves ammonia, and yields a sublimate of *ammoniated subchloride of mercury*, $2\text{Hg}_2\text{Cl}_2\text{NH}_3$; the residue, which is insoluble in water, and unchanged by boiling with alkalies, has a composition corresponding with the formula $\text{Hg}_2\text{Cl.Hg}_2\text{N}$ (that is, a double compound of nitride and subchloride of mercury).

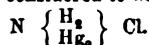
At a higher temperature, this compound evolves nitrogen, and leaves a residue of subchloride of mercury.

Amido-chloride of mercury is insoluble in water, but soluble in mineral acids; it is also soluble in free ammonia in the presence of the sulphate, nitrate, and acetate of ammonia, so that this reagent does not produce a precipitate in solutions of salts of oxide of mercury, containing a sufficient quantity of free sulphuric, nitric, or acetic acid. When boiled with water, amido-chloride of mercury is partly decomposed, assuming a yellow color.

White precipitate becomes yellow when treated with potassa, ammonia being evolved.

When ammonia is added to a very large excess of chloride of mercury, a compound is precipitated, which is expressed by the formula 3HgCl.HgNH_2 , and will be recognized as the chloride corresponding to the oxyamide of mercury,

¹ This compound might also be considered to be the *chloride of di-mercurammonium*,



Wagner's experiments have disposed him to regard it as a compound of chloride of mercury with *mercuramine*, $\text{HgCl.N} \left\{ \begin{array}{l} \text{Hg} \\ \text{H}_2 \end{array} \right\}$

$3\text{HgO} \cdot \text{HgNH}_2$. By increasing the proportion of ammonia, the other chloride ($2\text{HgO} \cdot \text{HgCl} \cdot \text{HgNH}_2$) of this series may be obtained.

Various compounds of amide of mercury (HgNH_2) with salts of oxide of mercury, have been obtained by the action of ammonia upon those salts.

The preceding compounds are interesting as forming one of the chief supports of the amidogen-theory of the constitution of ammoniacal salts.

§ 311. The *Bromides of Mercury* correspond in nearly all respects to the chlorides.

The *sub-bromide* Hg_2Br , is white, volatile, and insoluble.

The *bromide* HgBr , is soluble and crystallizable.

A black compound of sub-bromide with amide of mercury, $\text{Hg}_2\text{Br} \cdot \text{HgNH}_2$, is obtained by treating the former with ammonia.

An oxybromide, $\text{HgBr} \cdot 3\text{HgO}$, is also known.

SUBIODIDE OF MERCURY (Hg_2I) may be formed by triturating iodine with excess of mercury and a little alcohol; it is precipitated when an excess of nitrate of suboxide of mercury is added to iodide of potassium.

It has a dirty green color, and may be fused and sublimed without change, if rapidly heated; when heated slowly, however, it is decomposed into mercury and iodide of mercury; the alkaline iodides cause it to undergo the same decomposition, and dissolve the iodide formed.

IODIDE OF MERCURY, HgI .

Preparation.—This most beautiful substance may be prepared by triturating equal equivalents of mercury and iodine with a little alcohol, when the subiodide is formed at the same time. It is also easily obtained by adding chloride of mercury to a solution of iodide of potassium, when it is precipitated at first of a very light color, which quickly passes into a brilliant scarlet; in this experiment, the proportions employed must be carefully attended to, since the iodide is soluble in an excess of either reagent.

Properties.—Iodide of mercury ordinarily presents a splendid scarlet color, which is somewhat injured by exposure to light; when heated, it fuses easily to a red liquid, which afterwards sublimes in brilliant yellow crystals. The vapor of iodide of mercury is colorless, and is the heaviest gaseous substance known; its specific gravity is 15.68.

The yellow crystals gradually assume a scarlet color if left to themselves, but if rubbed with a hard body, they undergo this change immediately. Iodide of mercury is a dimorphous substance; the primitive form of the red modification is the square-based octohedron, while the crystals of the yellow variety are derived from the right rhombic prism.

Iodide of mercury is very slightly soluble in water, requiring 150 parts in the cold; it dissolves in alcohol, with the aid of heat, forming a colorless solution, from which, if slowly cooled, the iodide is deposited in the red modification; whereas, by rapid cooling, the yellow variety is obtained. It dissolves very readily in solution of iodide of potassium, forming a colorless solution; the best method of crystallizing the iodide of mercury consists in dissolving it, with the aid of heat, to saturation, in solution of iodide of potassium, which deposits it, on cooling, in fine scarlet crystals.

Iodide of mercury is capable of combining with several other iodides, and with some chlorides.

An intermediate iodide of mercury, of the formula $\text{Hg}_2\text{I} \cdot 2\text{HgI}$, is obtained as a yellow precipitate when nitrate of suboxide of mercury is precipitated by a solution of iodide of potassium containing free iodine.

An oxy-iodide of mercury, of the formula $\text{HgI} \cdot 3\text{HgO}$, has been obtained. When this compound is exposed to the action of dry ammonia, water is formed, together with a red-brown compound, $\text{HgNH}_2 \cdot \text{HgI} \cdot 2\text{HgO}$.

MERCURY AND SULPHUR.

Subsulphide	Hg ₂ S.
Sulphide	HgS.

SUBSULPHIDE OF MERCURY, Hg₂S.

§ 312. This compound may be obtained by gradually adding a solution of a salt of suboxide of mercury to a solution of an alkaline sulphide; it is a black precipitate which is exceedingly unstable, being decomposed, even when heated under water, into metallic mercury and the sulphide.

SULPHIDE OF MERCURY, CINNABAR, VERMILION, HgS.

This sulphide exists in the mineral kingdom, and is, in fact, the chief ore of mercury.¹

Preparation.—Sulphide of mercury is obtained as a black precipitate by the action of sulphuretted hydrogen, or a soluble sulphide, upon a solution of a salt of oxide of mercury.

There are several methods of obtaining vermilion on the large scale.

I. When 15 parts of sulphur are moderately heated with 95 parts of mercury, a black compound is formed, which is known as *Ethiops mineral*, and consists of a mixture of sulphide of mercury with an excess of sulphur; this mixture is subjected to sublimation, when the sulphide is obtained pure; when finely powdered with a little water, this sulphide forms the vermilion of commerce.

II. The most beautiful vermilion, however, is obtained in the moist way, by the action of solutions of the higher alkaline sulphides upon the black sulphides of mercury. 300 parts of mercury and 114 parts of sulphur are rubbed together in a mortar for two or three hours; 75 parts of hydrate of potassa and 400 parts of water are then added, and the whole kept for some hours at about 122° F. (50° C.), when the original black sulphide assumes a fine red color.

The theory of this operation is scarcely yet explained in a satisfactory manner.

III. If ordinary cinnabar be reduced to powder and heated for some time to about 122° F. (50° C.) with a solution of liver of sulphur, it is converted into a fine specimen of vermilion.

IV. At Idria, where the extraction of mercury from its ores is extensively carried on, vermilion is manufactured by a method similar to the first of those given above. 100 parts of mercury and 18 of sulphur are introduced into small wooden casks which revolve upon a horizontal axis; these casks are allowed to rotate for three or four hours, when the mercury is converted into black sulphide, which acquires a fine red color when sublimed and reduced to powder.

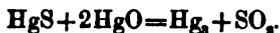
Properties.—Cinnabar, in its native state, is often associated with the sulphides of iron and copper; it is found sometimes in amorphous masses, sometimes crystallized in six-sided prisms, and varying in color from a dark brown to a bright red; it is occasionally transparent; it is brittle, and has the sp. gr. 8.098. When heated in close vessels, cinnabar sublimes, without previously fusing, and condenses again in six-sided prisms. If roasted in air, it burns, evolving sulphurous acid and vapors of metallic mercury.

Sulphide of mercury is insoluble in water; it dissolves only to a slight extent in hydrochloric or nitric acid, but readily in *aqua regia*.

When fused with alkalis or their carbonates, cinnabar loses its sulphur, and metallic mercury escapes; lime effects a similar reduction.

¹ Cinnabar has been found in a very pure state in California.

If sulphide of mercury be heated with oxide of mercury, the sulphur is oxidized at the expense of the latter, and the mercury of both compounds is separated in the metallic state:—



Carbon, hydrogen, copper, iron, tin, zinc, &c., are capable of reducing sulphide of mercury at a high temperature.

The sulphide of mercury, in the nascent state, is capable of combining with many of the salts of oxide of mercury, to form white compounds, which are obtained by adding a very small quantity of sulphuretted hydrogen to a solution of one of the salts in question; thus, if the sulphate of oxide of mercury be treated with a small quantity of sulphuretted hydrogen, a white precipitate is obtained, having the composition $\text{HgO SO}_4 + 2\text{HgS}$. Nitrate of oxide of mercury yields a similar compound. When the chloride of mercury is thus treated, the formula of the white precipitate is $\text{HgCl} + 2\text{HgS}$. These precipitates are all converted into black sulphide of mercury when treated with an excess of hydrosulphuric acid.

Vermilion is sometimes adulterated with minium, colcothar, brickdust, dragon's blood or realgar; the first three are left behind when the specimen is heated; the realgar may be detected by heating the vermilion with yellow sulphide of ammonium, and testing the filtered solution with excess of hydrochloric acid, which would precipitate yellow pentasulphide of arsenic. The presence of dragon's blood will be known by the empyreumatic odor evolved on heating, and by the red color which the specimen imparts to alcohol.

AMALGAMS.

§ 313. Mercury does not generally combine with those metals, such as iron, manganese, nickel, and cobalt, the fusing-points of which are very high; we find, however, an exception to this rule in platinum, which, in a finely divided state, is capable of amalgamating with mercury. The amalgams themselves are solid, but dissolve very readily in an excess of mercury; their fusing-points are very low. All amalgams are decomposed by heat, their mercury being volatilized.

At a slightly elevated temperature, mercury combines energetically with *potassium* and *sodium*, forming compounds which readily decompose water, the light metal being oxidized and dissolved, whilst the mercury separates.

These amalgams are employed for the preparation of the *amalgam of ammonium* (for the properties of which we refer to p. 135).

It is said that the amalgams of potassium, sodium, and ammonium, crystallize in cubes at a low temperature.

An amalgam of *iron* has been obtained by Joule, by precipitating that metal upon mercury by the electrotype process.

Mercury readily unites with *zinc*; when a plate of the latter metal is well cleaned with an acid, and rubbed with mercury, a very brilliant amalgam is formed upon its surface; zinc plates are thus treated when employed in the galvanic battery, in order to protect them in some measure from the action of the acid, since the latter acts much more slowly upon the amalgam than upon zinc itself.¹

An amalgam of 2 parts of zinc and 5 of mercury is used for the rubbers of electrical machines.

¹ Zinc plates may also be amalgamated by rubbing them with a solution of chloride of mercury acidified with hydrochloric acid.

According to Rose, the mercury precipitated by zinc from acid solutions of the sulphate and nitrate does not combine with the zinc.

Bismuth also combines very easily with mercury; an alloy of 1 part of bismuth with 4 of mercury, when shaken in a perfectly clean and dry glass vessel, coats the surface with a brilliant metallic film, giving it the aspect of a mirror.

Gold is immediately attacked by mercury; if a plate of gold be brought in contact with traces even of mercury-vapor, its surface is whitened. If it be rubbed with mercury, it becomes exceedingly brittle.

Mercury is capable of dissolving a large quantity of gold without losing its white color or its fluidity; when saturated with gold it is semisolid, and has a slightly yellow color; if the liquid amalgam be squeezed in a chamois leather, the mercury which passes through is found to contain very little gold, whilst the white pasty amalgam left on the filter is composed of about 2 parts of gold and 1 part of mercury.

Powdered gold, which is employed in painting, is prepared by dissolving 1 part of that metal in 8 parts of mercury, and distilling the amalgam, when the finely divided gold is left.

Mercury is not capable of acting upon compact *platinum*, only on the spongy metal; when the amalgam of platinum is treated with nitric acid, it dissolves, forming nitrate of oxide of mercury and nitrate of binoxide of platinum; it will be recollected that platinum itself is not attacked by nitric acid.

An amalgam of *copper* in which the proportion of the metals is represented by the formula CuHg , has been obtained by Joule, by retaining mercury in contact with the negative pole of a galvanic battery under solution of sulphate of copper, until that metal was fully saturated with copper.

The *amalgams of tin* possess some practical importance, since one of them is employed for silvering looking-glasses.

Mercury dissolves $\frac{1}{15}$ its weight of tin without much loss of fluidity; when the latter metal amounts to $\frac{1}{3}$ the weight of the mercury, the amalgam is soft and crystalline.

The *silvering of looking-glasses* with an amalgam of tin is thus effected. A sheet of tinfoil is smoothly spread upon a perfectly horizontal table, and its surface well rubbed with mercury; a thin layer of this metal is then poured uniformly over it, and the plate of glass slid on to it in such a way that its edge shall carry before it all the impurities upon the surface of the mercury; the glass is then weighted, and the table slightly inclined, to allow the superfluous mercury to run off as it is expressed; after some days, the amalgam is found firmly adhering to the glass; this amalgam is composed of about $\frac{1}{4}$ parts of tin and 1 of mercury.

Lead and mercury are exceedingly prone to enter into combination.

An *amalgam of silver*, AgHg_8 , has been found in nature, crystallized in dodecahedra.

Silver and mercury combine directly in almost all proportions; as in the case of gold, the liquid amalgams of silver, when strained, are separated into very rich solid, and very poor liquid amalgams; a continued red heat is required to expel the last traces of mercury from an amalgam of silver.

An amalgam of 15 parts of silver with 85 of mercury, is sometimes used for silvering copper and brass.

By submitting amalgams of various metals, in a suitable apparatus, to a pressure of 60 tons per square inch of surface, Joule has succeeded in expelling the excess of mercury from them, and has obtained definite amalgams, of which the formulæ are PtHg , AgHg_8 , CuHg , FeHg , Zn_2Hg , Pb_2Hg , Sn_2Hg .¹

¹ Crookewitt has examined certain definite amalgams to which he has assigned the formulæ AuHg_8 , BiHg , PbHg , CdHg_8 , $\text{Ag}_2\text{Hg}_{10}$, AgHg_8 , AgHg_6 , and AgHg_4 .

METALLURGY OF MERCURY.

§ 314. Mercury is sometimes found native in small globules disseminated throughout certain bituminous strata in the neighborhood of cinnabar.

Cinnabar, the sulphide of mercury, has been previously mentioned as the chief ore of this metal.

Subchloride of mercury is sometimes found in the mineral kingdom; it is commonly termed *horn-mercury*, and is occasionally crystallized in four-sided rectangular prisms.

An iodide of mercury has been found in Mexico.

EXTRACTION OF MERCURY.—The extraction of mercury is exceedingly simple, in consequence of the great volatility of the metal.

At Idria and Almaden, where the metal is chiefly extracted, the cinnabar is roasted, with free access of air, in reverberatory furnaces of a particular construction; the sulphur is oxidized and converted into sulphurous acid, while the mercury passes off in vapor, and is condensed, either by passing through a long series of earthenware adapters, or in brick chambers of considerable size; if any of the sulphide passes over unchanged, it is moulded into bricks with clay, or placed in saucers, and again roasted with the next charge of ore.

Mercury is also sometimes extracted by distilling the ore with iron or lime: in the latter case, sulphide of calcium and sulphate of lime are formed:—



If the ore itself contain a sufficient amount of limestone, as is sometimes the case, it is only requisite to moisten it with a little water, and to distil it. In any other case, the ore is mixed with a certain amount of slaked lime. The distillation is effected in iron retorts.¹

ASSAY OF THE ORES OF MERCURY.—The determination of mercury in a specimen of cinnabar is effected by mixing 100 grs. with 4 or 5 parts of dry carbonate of soda and about 10 parts of quicklime, heating the mixture in a hard glass tube placed in a combustion-furnace, and collecting the mercury which distils over; this may be washed with water by decantation, to remove any particles of lime, dried in the water-bath, and weighed. It will be found advantageous to place a little bicarbonate of soda at the closed end of the tube, so that by heating it at the conclusion of the operation, carbonic acid may be evolved, to sweep away all mercury-vapors out of the tube.

PHARMACEUTICAL PREPARATIONS OF MERCURY.—Mercury in various forms of combination is frequently used in medicine.

The red or nitric oxide, as it is termed, is sometimes applied externally. The suboxide has also been used.

Calomel is the principal form in which mercury is administered medicinally, and since it is termed by some chemists the chloride, and by others the subchloride of mercury, it would be well if its common name (*calomel*) were always retained in prescriptions, since a mistake between the two chlorides would be almost inevitably fatal.

¹ Violette recommends the application of high-pressure steam to the purification of mercury; he allows the steam to pass first through an iron worm, in which its temperature is raised to about 700° F., and then conducts it into an iron retort, in which is inclosed the vessel containing the mercury; the delivery-pipe, from which the steam issues, dips into the mercury.

The metal is thus raised to the proper temperature for distillation, and the resulting vapor rapidly removed from the retort by the steam, passing into an ordinary condensing-apparatus. This process appears to present many advantages over the ordinary process of distillation.

Corrosive sublimate (bichloride of mercury), in small doses, is an important remedial agent.

White precipitate, or *hydrargyri ammonio-chloridum*, is used as an external application.

Turbith or *turpeth mineral*, *hydrargyri oxydum sulphuricum*, see p. 458, is seldom employed.

The sulphide and the two iodides of mercury are found in the preparations of the Pharmacopœia.

Several preparations of mercury are employed medicinally, which are obtained by triturating metallic mercury with various substances which have no chemical action upon it, until globules of metal are no longer visible; examples of these are seen in blue pill, blue ointment, *hydrargyrum cum creta*, &c. It is yet undecided in what form the mercury exists in these preparations, some chemists asserting that they contain the metal itself, and others maintaining that it is present in the form of suboxide; the former opinion, namely, that the metal is present in a very finely divided state, seems the most feasible, for it is difficult to believe that a substance which has so feeble an affinity for oxygen at the ordinary temperature should be oxidized during the short period occupied by the trituration; perhaps only a part of the mercury is present in the form of suboxide.

Sal-alembroth is a mixture of corrosive sublimate with an equal weight of chloride of ammonium, which dissolves more readily in water than pure corrosive sublimate, in consequence of the formation of a double-salt.

LEAD.

Sym. Pb. Eq. 103.7. Sp. Gr. 11.445.

§ 315. The metal now before us is of great importance, because both itself and its compounds are, and have been from remote antiquity, applied to many useful purposes. The metallurgy of lead will, as usual, be discussed at the end of the section.

Preparation of Pure Lead.—In order to obtain this metal in a state of purity, nitrate of lead is calcined to expel the nitric acid, and the residual oxide of lead fused in a Hessian crucible lined with charcoal, when a button of pure metal is obtained.

Or precipitated sulphate of lead may be reduced by charcoal or nascent hydrogen (p. 172).

Properties.—Lead has a bluish-gray color, and when freshly cut, considerable lustre. It is exceedingly soft, may be easily scratched with the nail, or cut with a knife, and leaves a dark trace upon paper. Lead is very malleable, and may be beaten into thin leaves, but these are easily split, from the imperfect tenacity of the metal; for the same reason it cannot be drawn out into very fine wire; a wire of $\frac{1}{4}$ inch in diameter will not support more than 20 lbs.

Exposed to air, lead is soon tarnished, probably becoming covered with a film of suboxide.

If lead be prepared in a very finely divided state, it will be pyrophoric.

The oxide of lead is made by heating the dry tartrate of lead¹ in a glass

¹ The tartrate of lead is prepared by making solution of tartaric acid with a slight excess of ammonia, and adding to the solution an acetate of lead; the precipitate is washed with cold water.

tube (closed at one end, and constricted near the open end, so as to be readily sealed) as long as any fumes are evolved; the tube is then sealed with the blow-pipe flame. If the extremity of this tube be broken off, and the mixture of finely divided lead, with carbon, be scattered into the air, it burns with a red flash.

Heated in close vessels, lead fuses at about 635° F. (335° C.), and emits perceptible vapors at a red heat; however, it is not sufficiently volatile to be distilled. If fused lead be allowed to cool slowly, it crystallizes in octohedra.

Lead is often deposited in crystals, when slowly precipitated from its solutions by various metals; the so-called *Saturn's-tree* is obtained by suspending a bundle of zinc-turnings in a solution of acetate of lead, acidified with acetic acid, when the crystals of lead are deposited upon the zinc, giving it a pretty arborescent appearance.

When fused in air, lead oxidizes rapidly, becoming covered first with an iridescent pellicle, and subsequently with a yellow powder, which is litharge, or (prot-) oxide of lead; at a red heat the litharge fuses, and must be removed from the surface, if a continuous oxidation be required.

Lead is capable of dissolving a certain amount of oxide of lead, which renders it harder, hence the alteration in physical properties which the metal suffers when long fused in contact with air.

Pure lead is not affected by perfectly pure water (free from air), at the ordinary temperature; but if air be present, the metal is oxidized at its expense, and the oxide thus formed combines with the carbonic acid accompanying the air, to form a basic carbonate of lead, which is deposited as a coating of minute crystals upon the metal. The water will then be found to contain lead; but if saline matters (especially such as may yield insoluble lead-compounds, above all, the sulphates) be present in considerable quantity, no lead will be found in solution, for a film of an insoluble lead-salt (*e. g.* the sulphate) will be formed upon the surface of the metal, and will protect it from further oxidation.

Lead decomposes steam slowly, at a white heat, litharge being formed. It does not decompose water in presence of acids.

Lead is scarcely attacked by hydrochloric or dilute sulphuric acid; concentrated sulphuric acid dissolves it, with the aid of heat, as sulphate of lead, sulphurous acid being evolved:—



Concentrated nitric acid acts but slowly upon lead, a film of nitrate of lead, insoluble in that acid, being formed; dilute nitric acid, especially if heated, dissolves the metal rapidly, as nitrate.

LEAD AND OXYGEN.

Suboxide	Pb ₂ O
Oxide	PbO
Binoxide	PbO ₂

Intermediate oxides also exist.

SUBOXIDE OF LEAD, Pb₂O.

§ 316. This oxide is supposed by some chemists to compose the dark film which forms upon the surface of lead when exposed to air.

The suboxide may be prepared by heating oxalate of lead (PbO.C₂O₄), in an oil-bath, to about 572° F. (300° C.), as long as any gas (carbonic acid and carbonic oxide) is disengaged:—



Suboxide of lead is a black powder; when heated in close vessels to a temperature exceeding 700° F. (370° C.), it is decomposed into metallic lead and oxide of lead.

If heated in air, it burns, and is converted into the oxide.

Suboxide of lead is insoluble in water; acids and alkalis decompose it into oxide of lead, which dissolves, and metallic lead.

OXIDE, OR PROTOXIDE, OF LEAD, PbO. *Eq.* 111.7.

MASSICOT (*the oxide which has not been fused*).

LITHARGE (*crystalline oxide obtained by fusion*).

Preparation.—Some details relating to the preparation of this compound upon a large scale will necessarily be given when we describe the reduction of lead from its ores; suffice it for the present to say that it is produced by the oxidation of lead in air, under the influence of a high temperature.

Pure oxide of lead may be obtained by strongly heating the nitrate.

By dissolving oxide of lead in caustic soda, and slowly evaporating the solution, white dodecahedral crystals are obtained.

When hydrated oxide of lead is boiled with a quantity of potassa insufficient to dissolve it, it is converted into a brownish-yellow, crystalline anhydrous oxide, which becomes of a pale yellow color when heated.

If a solution of caustic soda be boiled with an excess of litharge, the clear liquid deposits, on cooling, rose-colored nearly cubical crystals of oxide of lead; if these be heated to dull redness, and allowed to cool slowly, they remain red, but if suddenly cooled, become yellow.

Properties.—From what we have said above, it will be seen that the physical properties of the oxide of lead differ much according to the method of preparation; thus it may vary in color from white to red or yellow; all these varieties occur in the litharge of commerce, which often contains traces of silver, and occasionally of copper. The different varieties of the oxide give, when powdered, a product having the ash-gray color of litharge.

Oxide of lead, as obtained by the calcination of the nitrate, has a yellow color, which becomes darker, and ultimately brownish-red on heating; it fuses at an intense red heat, and is somewhat volatile at a very high temperature. On cooling from the fused state, it crystallizes in shining plates (litharge). The true primitive form of oxide of lead appears to be the octohedron with a rhombic base.

When exposed to air, it slowly absorbs carbonic acid. Heated in air to about 572° F. (300° C.) it absorbs oxygen, and is converted into minium, a compound of oxide with binoxide of lead.

Oxide of lead is slightly soluble in pure water; about 7000 parts of the latter take up 1 part of oxide of lead; the solution has an alkaline reaction. The presence of a small quantity of saline matter hinders the solution of the oxide. Water holding sugar in solution is capable of dissolving a considerable quantity.

Oxide of lead is a powerful base, forming numerous well-defined salts. The soluble neutral salts have an acid reaction. It is also capable of dissolving in alkaline solutions, forming compounds, some of which are crystallizable, and have received the name of *plumbites*, though the powerful basic properties of the oxide of lead appear to forbid the supposition that it should ever be capable of playing the part of an acid; these are more probably double compounds similar to those which we occasionally see formed between powerful bases.

Oxide of lead is very easily reduced by hydrogen or carbon, with the aid of heat. Silicic acid, at a high temperature, readily combines with oxide of lead;

hence litharge should not be fused in earthen crucibles, since it corrodes them rapidly.

Oxide of lead is isomorphous with baryta and lime, which, indeed, in many of its chemical relations, it much resembles.

Uses.—Litharge is employed in preparing white-lead, in the manufacture of glass, and in glazing some kinds of earthenware. A compound of litharge with lime is sometimes used for dyeing the hair of a purplish-black color; the color is due to the production of sulphide of lead from the sulphur existing in hair.

It is also an important reagent in assaying.

Hydrated oxide of lead, PbO.HO , is obtained as a white crystalline precipitate when a solution of a lead salt is decomposed by a caustic alkali; it is easily dehydrated by heat, and dissolves in the alkalies.

NITRITE OF LEAD, PbO.NO_2 .—This salt is prepared by passing carbonic acid through an aqueous solution of basic nitrite of lead, filtering off the carbonate of lead which is precipitated, and evaporating the solution, when yellow prismatic crystals of the nitrite are deposited.

Nitrite of lead is employed for preparing other nitrites by double decomposition.

Basic nitrite of lead, $4\text{PbO.NO}_2.\text{HO}$, is obtained by boiling a solution of nitrate of lead for a considerable period with an excess of metallic lead. It is a crystalline salt of a pink color; its solution has a very alkaline reaction.

Another basic nitrite, $2\text{PbO.NO}_2.\text{HO}$, is deposited in yellow needles when the salt 2PbO.NO_2 is boiled with metallic lead.

NITRATE OF LEAD, PbO.NO_3 .

Preparation.—In order to prepare this salt, metallic lead, the oxide, or its carbonate is dissolved in nitric acid, and the solution allowed to crystallize.

Properties.—Nitrate of lead crystallizes in hard anhydrous octohedra, which are sometimes transparent and sometimes opaque. They are unalterable by exposure to air. When heated, nitrate of lead decrepitates, fuses, and is decomposed into oxide of lead, which remains behind, whilst peroxide of nitrogen and oxygen are evolved:—



Nitrate of lead is somewhat sparingly soluble in water, 1 part of the salt requiring about 7 parts of cold water; it is more soluble in hot water. This salt is almost insoluble in nitric acid; hence, when alloys containing lead are treated with that solvent, a considerable quantity of water should be added after the oxidation is completed, in order to insure the solution of the nitrate of lead.

Nitrate of lead is used in the laboratory for the preparation of peroxide of nitrogen; it is also occasionally employed as a reagent.

Three basic nitrates of lead have been obtained.

$\text{PbO.NO}_3.\text{PbO.HO}$ is obtained in colorless crystals when a solution of nitrate of lead is boiled with oxide or carbonate of lead, and the filtered liquid allowed to cool.

$\text{PbO.NO}_3.3(\text{PbO.HO})$ is produced when the neutral nitrate is treated with a slight excess of ammonia; if digested with a large excess of ammonia, the hydrated oxide of lead is obtained.

The other nitrate contains 6 eqs. PbO , and is prepared by partially decomposing the neutral nitrate with ammonia.

Two compounds of nitrate with nitrite of lead are known; they are prepared by dissolving lead in a solution of the nitrate.

If a very dilute solution of nitrate of lead be digested at about $158^\circ \text{F. (70}^\circ \text{C.)}$ with a quantity of metallic lead in the proportion of 1 eq. for each equivalent of nitrate, the metal is gradually dissolved, forming a yellow solution, which,

on cooling, deposits brilliant yellow plates having the composition $2\text{PbO}\cdot\text{NO}_3$, $2\text{PbO}\cdot\text{NO}_2 + 2\text{HO}$.



When treated with strong acids, these crystals evolve red vapors.

If, in the above experiment, 3 eqs. of lead be employed for every 2 eqs. of the nitrate, the solution deposits crystals of an orange salt, much less soluble than the yellow compound, and having the composition $4\text{PbO}\cdot\text{NO}_3$, $3\text{PbO}\cdot\text{NO}_2 + 3\text{HO}$.

Those chemists who regard the compound NO_2 as hyponitric acid, consider these basic salts as *hyponitrates of lead*, having the formula, respectively, $2\text{PbO}\cdot\text{NO}_2 + \text{HO}$, and $7\text{PbO}\cdot 2\text{NO}_2 + 3\text{HO}$; but this view is contradicted by the circumstance that when acted on by alkalies, these compounds yield mixtures of nitrates and nitrites.

SULPHATE OF LEAD, $\text{PbO}\cdot\text{SO}_4$.

This salt is found in nature crystallized in translucent octohedra, called by mineralogists *lead-vitriol*.

Preparation.—A solution of nitrate or acetate of lead is precipitated by dilute sulphuric acid, the precipitate washed, first by decantation, afterwards upon a filter, till the washings have no longer an acid reaction.

A large quantity of sulphate of lead is obtained as a by-product in the preparation of acetate of alumina (for dyeing), by decomposing sulphate of alumina with acetate of lead.

Properties.—Sulphate of lead is a white solid; it is the only sulphate of a heavy metallic oxide which is not decomposed by a high temperature; it is very sparingly soluble in water, and in dilute sulphuric acid; it is soluble, however, to a considerable extent, in concentrated sulphuric acid, and is precipitated on adding water. It is also very perceptibly soluble in concentrated and diluted nitric acid; hydrochloric acid, with the aid of heat, dissolves it in the form of chloride of lead, which is deposited on cooling, while free sulphuric acid is found in the solution; it is insoluble in alcohol.

Sulphate of lead is decomposed and dissolved by the fixed caustic alkalies; when boiled with carbonates of potassa and soda, it yields insoluble carbonate of lead and alkaline sulphates. The decomposition is more easily effected by fusion; the soluble sulphides also decompose sulphate of lead.

The reduction of sulphate of lead is easily effected by carbon, hydrogen, or carbonic oxide, at a high temperature.

When strongly heated with an excess of carbon, it is reduced to sulphide of lead, but if gradually heated, sulphurous acid is disengaged, and subsulphide of lead, Pb_2S , remains: $2\text{PbO}\cdot\text{SO}_4 + \text{C}_2 = 3\text{CO} + \text{SO}_2 + \text{Pb}_2\text{S}$.

If sulphate of lead be heated with only so much carbon as is required to reduce the oxide of lead, and to convert the sulphuric acid into sulphurous, metallic lead is obtained; but if half this quantity be employed, we obtain the oxide of lead, the sulphur being disengaged in the form of sulphurous acid.

Sulphate of lead may be reduced to the metallic state by zinc, in presence of water acidulated with sulphuric or hydrochloric acid, when the nascent hydrogen is probably the true reducing agent: this reaction is sometimes turned to advantage in preparing pure lead for cupellation.

A partial decomposition is suffered by sulphate of lead when strongly heated in an earthen crucible, a little silicate of lead being formed.

The reduction of sulphate of lead may be effected by strongly heating it in

¹ According to Kuhn, when ammonia acts upon freshly precipitated sulphate of lead, the compound $2\text{PbO}\cdot\text{SO}_3$ is produced.

contact with sulphide of lead; if 1 eq. of the sulphate be heated with 1 eq. of sulphide, all the lead is reduced:—



when 2 eqs. of sulphate are employed, two-thirds of the lead remain as oxide:—



We shall hereafter see these reactions turned to account in the reduction of lead from its ores.

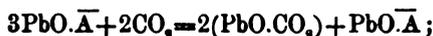
CARBONATE OF LEAD, CERUSE, WHITE LEAD, PbO.CO_2 .

§ 317. The carbonate of lead (*lead-spar* or *white-lead-ore*) is found native, generally associated with galena; it occurs in transparent crystals, having the same form as those of arragonite, and possessed of the property of double refraction.

The action of air, containing aqueous vapor and carbonic acid, upon metallic lead, gives rise to the production of an incrustation, often of considerable thickness, which is composed of carbonate and hydrated oxide of lead; the formation of this crust is much promoted by the presence of organic matters (which yield carbonic or other acids by their decomposition). This corrosion of lead has been observed to be particularly active in situations where portions of lead-roofing are exposed to the action of the vitiated air issuing from a crowded apartment. Pieces of lead (*e.g.* bullets) which have been cast in moulds smeared with oil, have been known to become coated with carbonate, even in a few weeks. The presence of unstable organic matters in most river and well-waters, will help to explain their rapid action upon leaden cisterns. It is remarkable that (as in the rusting of iron) when the superficial conversion of lead into carbonate has once commenced, it proceeds with comparative rapidity throughout the mass, perhaps because a voltaic couple is formed by the metal and its coating of carbonate.

Preparation.—On the small scale, it is prepared by precipitating a solution of acetate of lead with excess of carbonate of soda; the precipitate is collected on a filter, and washed.

For the purposes of the arts, carbonate of lead is manufactured by decomposing the tribasic acetate of lead with carbonic acid:—



this principle may be carried out in various ways.

The old (*Dutch*) process consists in suspending rolls¹ of sheet lead in earthen pots, into which a small quantity of inferior vinegar is poured; this is not permitted to come in contact with the lead; the pot is then partially covered with a sheet of lead, and several thus prepared are arranged in alternate layers with dung or spent tan, and completely buried in a heap of the same refuse, so constructed as to admit of a free passage of air. After some weeks, the heap is destroyed, when the metal is found coated with a thick incrustation of white-lead, which must be detached, washed, ground into a paste with water and dried in porous earthen pots at a moderate heat.

The theory of this process is very simple; the lead, in contact with air and vapors of acetic acid, is oxidized and converted into tribasic acetate of lead, which is decomposed by the carbonic acid disengaged in the fermentation of the heaps, yielding carbonate and neutral acetate of lead (*see the above equation*); the latter is capable of combining with a fresh portion of oxide of lead, thus reproducing the tribasic acetate, again to undergo the same process; thus, a very small quantity of vinegar would suffice to produce a very considerable quantity of car-

¹ Gratings of lead are now generally employed instead of rolls. These are made of the purest lead to be found in commerce.

bonate of lead; a little acetate of lead of course remains in the white lead at the end of the process, but is removed by washing; moreover, the carbonate, when formed, always combines with more or less hydrated oxide of lead. The operation is considerably accelerated by the heat disengaged in the fermentation of the heap, causing the production of large quantities of acetic acid vapor in the pots.

This process had been in use for a very long time before it was discovered that it might be carried out in a far simpler manner by boiling an excess of litharge with acetic acid, and passing a current of carbonic acid through the tribasic acetate of lead thus obtained, when carbonate of lead is precipitated, carrying with it a variable amount of hydrated oxide, and a solution of neutral acetate produced, which needs only to be boiled with more litharge, in order to reproduce the tribasic acetate. The carbonic acid employed for this purpose is usually that produced in the combustion of the fuel used for the boilers. Occasionally, the process is modified by passing the carbonic acid over litharge moistened with acetic acid, or with a weak solution of acetate of lead.

It is sometimes objected, however, that the white lead prepared by these new processes has not so good a *body* as the old product.

The white lead of commerce always contains a considerable quantity of hydrated oxide of lead; the analyses of many specimens of this product have shown that it is generally a *basic carbonate* of the formula $2(\text{PbO} \cdot \text{CO}_2), \text{PbO} \cdot \text{HO}$; other specimens have been found to correspond to the formula $3(\text{PbO} \cdot \text{CO}_2), \text{PbO} \cdot \text{HO}$.

Properties.—Carbonate of lead is a white substance, which is easily decomposed by heat into carbonic acid and (prot-) oxide of lead, which, if not too strongly heated, absorbs oxygen, and is converted into minium (red lead). It is insoluble in water, but dissolves in solution of carbonic acid, and in all acids which form soluble compounds with its base; carbonate of lead is also soluble in the fixed alkalis.

Sulphuretted hydrogen easily decomposes carbonate of lead, ultimately converting it into black sulphide of lead; hence arises the dark color acquired by lead-paints when exposed to a foul atmosphere.

Carbonate of lead is a very powerful poison

Uses.—Great use is made of this compound in painting, and it is hence an important article of commerce. It is sometimes adulterated with sulphate of lead, sulphate of baryta, chalk, and plaster of Paris. To detect these impurities, the specimen should be heated with an excess of acetic acid; the solution saturated with sulphuretted hydrogen, filtered, and tested for lime with oxalic acid; the production of a precipitate indicates adulteration with chalk. The residue left by acetic acid may contain sulphate of baryta, sulphate of lead, and sulphate of lime (plaster of Paris); it should be washed, and boiled with dilute hydrochloric acid, which dissolves the last two; a part of the (hot) solution may be set aside to cool, when crystals of chloride of lead will be deposited if any sulphate has been dissolved by the hydrochloric acid; the other portion may be mixed with excess of ammoniac and sulphide of ammonium, the sulphide of lead filtered off, and the solution tested for lime with oxalate of ammonia; the presence of sulphate of baryta will be known by the insolubility of the residue after repeatedly boiling with dilute hydrochloric acid.¹

¹ This compound is also obtained when an alkaline carbonate is added to a boiling solution of litharge.

² When the white lead is mixed with chalk it becomes more difficult to ascertain the exact nature of the solution, and since the methods which must be adopted in order to destroy the carbonate of lead by means of acetic acid, and gradually adding dilute hydrochloric acid, will not give us the terms of combination in which the sulphate of lead is present, it is necessary to identify the differ-

Carbonate of lead is employed for glazing cards, which consequently become black when exposed to sulphuretted hydrogen; in fact, cards covered with carbonate of lead will indicate very small quantities of this gas.

In chemical investigations carbonate of lead is sometimes employed to remove sulphuric or hydrosulphuric acid from solutions or gases; for the former purpose it is better to prepare it expressly, and to keep it in a moist state till required for use.

Compounds of sulphate of lead with 1 and 3 eqs. of carbonate of lead form minerals called, respectively, *lanarkite* and *leadhillite*.

Silicic acid and oxide of lead enter into the composition of various kinds of glass; the *silicates of lead* are easily fusible, especially if they contain a large amount of base; in the latter case, the silicate has a yellow or brown color, whilst, if the silica predominate, it is colorless.

CHROMATES OF LEAD. NEUTRAL CHROMATE OF LEAD. CHROME-YELLOW.



This chromate is found (though rarely) in the mineral kingdom, as *red-lead-ore of Siberia*; it is crystallized in prisms. It is formed by the action of chromate of potassa on sulphate or carbonate of lead, in the cold.

Preparation.—It is prepared by decomposing acetate of lead with chromate of potassa, when it falls as a fine yellow precipitate:—



the tint of the precipitate varies with the temperature at which it is formed, and according to the state of neutrality of the solutions; these latter are employed in a rather dilute state, to avoid the formation of a crystalline compound which appears to be a double-salt.

Properties.—Chromate of lead has a very fine yellow color; when heated, its color changes to a red-brown; it fuses at a red heat into a grayish-brown mass, and subsequently evolves oxygen, and is converted into a mixture of sesquioxide of chromium and a basic chromate of lead:—



Chromate of lead is insoluble in water, sparingly soluble even in nitric acid, but readily so in potassa.

Uses.—It is employed, to a great extent, in painting and calico-printing; the commercial chromate is sometimes mixed with sulphate of lime, which improves its color.

Chromate of lead is very much used in the analysis of organic substances; when heated to bright redness with compounds containing carbon and hydrogen, it readily oxidizes these elements, converting them into carbonic acid and water, forms in which their weight may be conveniently determined; if sulphur be present, it remains behind as sulphate of lead, which is a great advantage in the use of chromate of lead instead of oxide of copper, for combustion. Previously to being used for this purpose, the chromate is fused, in order to expel all traces of moisture.

BIBASIC CHROMATE OF LEAD. DICHROMATE OR SUBCHROMATE OF LEAD.



This salt is always formed when the neutral chromate is treated with a quantity of alkali insufficient to decompose it; it is also deposited in red crystals

ent acids and bases; the quantities of these will, however, guide him in his conclusions as to the really important adulteration. Probably, by powerful pressure in blotting-paper, between hot iron plates, the oil might be so far extracted as to allow of the application of the ordinary method of testing.

when carbonic acid is passed through a solution of oxide of lead and chromate of lead in caustic potassa.

A product having a very beautiful red color, is obtained by gradually adding chromate of lead to fused nitre, allowing the basic chromate to subside, pouring off the supernatant fused mass, and rapidly washing the basic salt; the potassa of the nitre here abstracts one-half of the chromic acid from the neutral lead-salt.

The fine red color of this basic chromate renders it useful in calico-printing; it is usually produced by immersing the stuff, previously printed with the neutral chromate in a bath of lime-water (or other weak alkaline liquor), which converts the chromate into dichromate.

A *sesqui-basic chromate of lead* ($3\text{PbO} \cdot 2\text{CrO}_3$) occurs in nature as *melano-chroite*.

BINOXIDE OF LEAD, PURE OXIDE OF LEAD, PLUMBIC ACID, PEROXIDE OF LEAD, PbO_2 .

§ 318. This oxide is found in the mineral kingdom as *heavy lead-ore*; it is formed when the (prot-) oxide of lead is treated with very powerful oxidizing agents; thus, if litharge be gently heated with one-fourth of its weight of chlorate of potassa, and the fused mass washed with boiling water, binoxide of lead is left; again, it may be obtained by suspending the (prot-) oxide in water, and passing a current of chlorine, or, equally well, by treating a solution of acetate of lead with an alkaline hypochlorite; in this way, it is sometimes obtained in a crystalline state.

The following, however, is the best method of preparing the binoxide of lead.

Minium (red-lead), in fine powder, is boiled with an excess of dilute nitric acid, the mixture being constantly stirred; the solution (containing nitrate of lead) is decanted, the residue (binoxide of lead) boiled with water, and washed until the washings are no longer affected by hydrosulphuric acid; it is then dried in a water-bath.

Properties.—Binoxide of lead has a dark purplish-brown color; the native variety forms iron-black, lustrous, six-sided prisms. When heated, it is easily decomposed, evolving oxygen, and yielding, first, an intermediate oxide, and ultimately litharge.

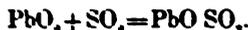
It is insoluble in water and in acids in the cold; nitric acid (as we have seen) is incapable of dissolving it, even with the aid of heat; if it be heated with sulphuric acid, it parts with half of its oxygen, being reduced to (prot-) oxide of lead, which combines with the acid:—



hydrochloric acid converts it into chloride of lead, with evolution of chlorine:—



Binoxide of lead is a powerful oxidizing agent; it eagerly absorbs sulphurous acid, with great disengagement of heat, and is converted into sulphate of lead:—



This property renders it useful in the laboratory for removing sulphurous acid from gaseous mixtures, especially in organic analysis.

When ammoniacal gas is passed over the binoxide of lead, the latter is partially reduced, water and nitrate of ammonia being formed.

Binoxide of lead is capable of combining with bases to form definite, and, in some cases, crystallizable salts termed *peroxidates*.

The *potassic peroxide* is prepared by fusing plumbic acid with hydrate of potassa in a silver crucible; it dissolves in a boiling alkaline solution, and may be crystallized in colorless cubes the formula of which is $\text{KO} \cdot \text{PbO}_2 \cdot 3\text{HO}$; water decomposes this salt, and plumbic acid is precipitated.

MINIUM, RED LEAD, PLUMBATE OF OXIDE OF LEAD.

This substance varies in composition according to the circumstances under which it is obtained.

When a solution of oxide of lead in potassa is added to plumbate of potassa, a yellow precipitate of hydrated minium is formed.

Preparation.—Minium is prepared on the large scale by heating lead in a reverberatory furnace to a temperature insufficient to fuse the oxide which is formed, and subsequently heating this oxide (massicot), with free access of air, to a temperature not exceeding 572° F. (300° C.), when it is converted into minium; the roasting is generally repeated two or three times before the oxidation is complete.

The massicot obtained by heating ordinary impure lead in air varies in quality; the product first formed contains the oxides of those metals which are more readily oxidizable than lead, whilst that last obtained is contaminated with those metals which are less easily oxidized, such as copper and silver; the massicot produced in the middle of the process is the purest, and is preferred for the manufacture of minium.

If the lead employed should contain any manganese, permanganate of lead will be found in the minium.

An orange variety of minium is obtained by gently heating carbonate of lead in air.

Properties.—The minium obtained by heating massicot in air till no further increase of weight is observed, has the composition $2\text{PbO} \cdot \text{PbO}_2$, and this formula would appear to represent the true minium, the others being probably mixtures of this substance with oxide of lead, which is dissolved out by acetate of lead, or by potassa, the above compound being left. Crystals of minium which were accidentally formed in a furnace, were found to contain $3\text{PbO} \cdot \text{PbO}_2$; and Mulder has recently assigned this formula to the greater number of specimens of minium. A specimen of minium analyzed by Berzelius contained $\text{PbO} \cdot \text{PbO}_2$; the same compound was obtained by Winkelblech, by adding hypochlorite of soda to a solution of oxide of lead in potassa.

All the intermediate oxides of lead, however, possess a more or less intense red color; they evolve oxygen when strongly heated, leaving the (prot-) oxide of lead.

When treated with acids, the miniums behave just as combinations of the oxide and binoxide of lead would be expected to; thus nitric acid leaves binoxide of lead undissolved; hydrochloric acid yields free chlorine, &c.

Uses.—Minium is employed largely in the arts, being the commonest red mineral color. It is also used in the fabrication of glass, where the oxygen which it disengages when heated serves to remove any carbonaceous matters which may accidentally be present.

The red-lead of commerce is sometimes adulterated with earthy substances (brickdust) and colcothar.

CHLORIDE OF LEAD, PbCl_2 .

§ 819. This chloride, which is found native as *horn-lead*, may be formed by the direct combination of its elements at a red heat.

It is prepared by decomposing a concentrated solution of a lead-salt with hydrochloric acid or a soluble chloride, when chloride of lead is precipitated.

It has a white color, and readily fuses when heated; at a high temperature, it is capable of volatilization. Fused chloride of lead resolidifies into a gray horny mass, known by the ancients as *horn-lead*.

Chloride of lead is very sparingly soluble in water; 1 part of the salt requires

135 parts of cold, and 33 of boiling water; it is more soluble in hydrochloric and nitric acids; it is deposited from its solutions, on cooling, in hexahedral prisms. It is insoluble in alcohol.

The alkalis and their carbonates, added in small proportion, convert it into oxychloride of lead, while a larger quantity decomposes it entirely.

OXYCHLORIDES OF LEAD.

When chloride of lead is heated in air till no more fumes are evolved, the compound $PbCl, PbO$ is formed.¹

Oxide and chloride of lead appear to be capable of combining in several proportions; hence the composition of the compound commonly called *oxychloride* is variable, but the most general formula appears to be $PbCl.7PbO$. Two oxychlorides exist in nature, having the composition $PbO.PbCl$, and $2PbO.PbCl$ (*mendipite*).

The oxychloride of lead is prepared either by fusing 1 part of the chloride with 6 or 8 parts of litharge, by heating 10 parts of litharge with 7 of sal-ammoniac, or by boiling with water a mixture of litharge and $\frac{1}{4}$ its weight of chloride of sodium, when a white hydrated oxychloride is formed, which assumes a yellow color on calcination.

A method recently introduced for the preparation of the oxychloride consists in decomposing the chloride with lime-water.

The compound obtained by the first process varies in composition according to the proportions employed; that obtained by the second, has the formula $PbCl.7PbO$. The third process yields $PbCl.3PbO.HO$.

Oxychloride of lead ($PbCl.7PbO$) has a fine golden-yellow color, and is very fusible; when resolidifying, it crystallizes in octohedra.

It is used as a pigment under various names, such as *mineral yellow*, *Turner's yellow*, *Paris yellow*.

Bromide of Lead resembles the chloride.

Iodide of Lead (PbI) is obtained in fine lustrous yellow scales on mixing boiling solutions of iodide of potassium and acetate of lead, and allowing the mixture to cool.

Iodide of lead forms double-salts with the alkaline iodides; it also gives a crystalline compound with chloride of ammonium.

A blue *oxy-iodide of lead* exists.

SULPHIDE, OR SULPHURET, OF LEAD, PbS .

§ 320. This sulphide occurs abundantly in nature, in the form of *galena*, which is almost the only ore of lead worth smelting.

There are two varieties of galena, the compact and micaceous, differing in their external appearance, the latter presenting numerous small facets which sparkle in the light; this variety often contains a considerable quantity of silver, and is then termed argentiferous galena.

Galena has a dark gray color, and metallic lustre; its specific gravity is 7.585, and the primitive form of its crystals is the cube. Galena fuses at a higher temperature than lead, and may be volatilized in a current of gas; it loses a little sulphur when strongly heated. If heated in air, galena is converted into a mixture of oxide and sulphate of lead, sulphurous acid being evolved.

Dilute sulphuric and hydrochloric acids have scarcely any action upon the

¹ Pattinson has proposed this compound in a hydrated state as a substitute for white lead; he prepares it by decomposing a hot solution of chloride of lead with lime-water, when a white precipitate is produced, the formula of which is $PbCl.PbO.HO$.

sulphide of lead; concentrated sulphuric acid converts it into sulphate of lead, with evolution of sulphurous acid:—



it is also attacked by long boiling with concentrated hydrochloric acid.

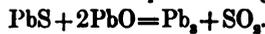
When treated with concentrated nitric acid, sulphide of lead is entirely converted into the insoluble sulphate; whereas, if dilute nitric acid be employed, part of the sulphide is converted into sulphate, while the remainder is decomposed, nitrate of lead being found in solution, and sulphur separated.

The alkalis and alkaline earths, when fused with sulphide of lead, give rise to a separation of metallic lead, the sulphur combining with the alkali-metal, which parts with its oxygen to a portion of the sulphide of lead; a slag is thus formed containing sulphate of lead, sulphide of lead, and the sulphide of an alkali-metal.

Many substances are capable of oxidizing a part of the sulphur contained in sulphide of lead, thus causing a separation of metallic lead. In this way, a certain quantity of nitre, when fused with sulphide of lead, separates a portion of metal. The oxides of iron, manganese, and copper have the same effect.

When steam is passed over sulphide of lead at a high temperature, the oxygen is converted into sulphurous acid, and the hydrogen into hydrosulphuric acid, metallic lead being eliminated.

Sulphide of lead may also be reduced (as is effected on the large scale in the smelting of lead-ores) by fusion with 2 eqs. of litharge:—



Hydrogen, iron, copper, zinc, and tin are capable of reducing sulphide of lead at a high temperature.

Sulphide of lead may be obtained artificially by fusing sulphur with metallic lead, or by the action of sulphuretted hydrogen upon a solution containing that metal; in the latter case, it forms a black precipitate.

A red compound of chloride with sulphide of lead is precipitated when sulphuretted hydrogen is passed into a solution of chloride of lead in hydrochloric acid.

Selenide of Lead (PbSe) occurs associated with the sulphide in certain lead-mines; it much resembles galena, with which it is isomorphous. Selenide of lead is employed as a source of selenium.

Lead is capable of combining with almost all other metals, but since these compounds are not of a very definite character, we shall only consider them, with reference to their practical utility, in the section devoted to the technical history of lead.

METALLURGY OF LEAD.

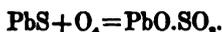
§ 321. Lead occurs in nature in a variety of combinations, of which the following are the most important:—

<p>(Prot-) oxide, { pure, and in combination with alumina.</p> <p><i>Minium</i></p> <p><i>Oxychloride</i></p> <p><i>Sulphide</i>, { pure, and associated with other metallie sulphides, as those of silver and antimony.</p> <p><i>Sulphate</i></p> <p><i>Selenide</i></p> <p><i>Telluride</i></p>	<p><i>Arseniate</i> (mixed with chloride of lead)</p> <p><i>Phosphate</i> " "</p> <p><i>Arsenide</i></p> <p><i>Carbonate</i> (with lead-ore)</p> <p><i>Carbonate</i> (mixed with chloride)</p> <p><i>Chromate</i></p> <p><i>Vanadate</i></p> <p><i>Tungstate</i></p> <p><i>Molybdate</i>, &c.</p>
--	---

We have already remarked that the metal is almost invariably extracted from the sulphide

EXTRACTION OF LEAD.—Galena is sometimes reduced by iron, at a high temperature, in a reverberatory furnace, but far more commonly by the *method of reaction*, as it is termed, in which the following chemical changes are taken advantage of:—

1. When sulphide of lead is roasted in air, it is converted into sulphate of lead:—



2. Sulphide of lead, in contact with 3 eqs. of sulphate of lead at a high temperature, is decomposed according to the equation:—



3. The sulphide, heated with 1 eq. of sulphate of lead, yields sulphurous acid and the metal:—



4. 1 eq. of sulphide of lead with 2 eqs. of the oxide, also yield the metal:—



After the galena has been freed from gangue, it is broken up into small fragments, and roasted on the hearth of a reverberatory furnace fed with coal; the ore is frequently stirred with a rake to expose fresh portions to the oxidizing action. Since the rapid current of air which traverses the hearth is liable to carry away a considerable quantity of lead (and silver), several condensing chambers are arranged between the furnace and the chimney, to avoid loss from this cause.

When the roasting has been continued for a sufficient period, the temperature is raised considerably, when the oxide and sulphate of lead react upon the unaltered sulphide, causing a separation of metallic lead, and of a very fusible sub-sulphide. The fire is now damped, and some quicklime thrown on to the fused mass; this causes the solidification of the slag (by forming a less fusible silicate of lime), and allows the lead to be drawn off into the pig-moulds. The slag is smelted in another operation, either alone, or together with a fresh charge of ore.

The lead thus obtained often contains enough silver to pay for extraction, which is effected either by cupelling it directly, or after subjecting it to a refining process. This latter is always had recourse to when less than $\frac{1}{100}$ of silver is present.

The refining process (Pattinson's) consists in fusing the metal, and allowing it to cool in an iron pot, stirring it from time to time with an iron rod; a portion of the lead (containing comparatively little silver) is soon deposited in crystals, which may be removed with a perforated ladle; by repeating this process, both with the liquid and solid portions, the lead is separated into two products, the one so poor in silver that it may be sent into the market, and the other sufficiently rich to be purified by *cupellation*, wherein the superior oxidability of lead is taken advantage of in order to separate it from the silver.

The *cupel* from which this process derives its name is a shallow cup, made of well-burnt bone-ashes rammed into an iron frame; the cupelling-furnace is a reverberatory furnace, the arch of which is formed by a movable dome of iron: an opening (for removing the litharge) is made near the edge, on one side of the cupel, and opposite to this are one or two tuyère pipes, through which air may be forced over the surface of the metal.

The lead is introduced into the cupel, through the arch of the furnace, in a melted state, and a fresh supply added as it diminishes in quantity; when the metal is brought to a full red heat, a blast of air is directed over its surface; a black film of suboxide (?) is first formed, and removed by the workman; by and by, the heat is increased, and the surface of the lead becomes covered with

litharge, which fuses, and is removed from the surface, partly by the action of the blast air, partly by the aid of a workman; the first litharge is impure (page 470), and is collected separately; the operation is continued, the stream of air being gradually increased, until the oxidation of the lead is completed; the litharge obtained in the latter part of the process being received separately, since it contains a considerable quantity of silver; the last portions of the litharge are absorbed by the cupel. The termination of the process is indicated by two appearances in the residual mass of metal; this mass has been hitherto maintained at a more brilliant temperature than the surrounding parts of the cupel, in consequence of the heat evolved during the oxidation of the lead, but this being completed, the metal assumes the same temperature and aspect as the cupel itself; again, towards the end of the operation, the film of litharge gradually becoming thinner, presents the phenomenon of iridescence, and finally vanishes entirely. The workman observing these appearances, pours a quantity of water on to the metal, and removes the disk, which consists of silver containing about $\frac{1}{8}$ of lead, which is separated from it by a method to be described hereafter (*see* Extraction of Silver).

This mass of silver sometimes presents a very peculiar appearance, as of arborescent branches, sometimes of considerable length, springing from its upper (convex) surface (*sprouting*); this is caused by the remarkable property possessed by silver, of absorbing, when in the fused state, a quantity of oxygen, which escapes, throwing up portions of the metal, as the mass cools.

The litharge obtained in the cupelling process is reduced by heating with charcoal.

Another method of desilverizing lead consists in fusing it with metallic zinc, which is found to be capable of removing the silver from argentiferous lead. The zinc is afterwards separated by distillation, and the silver (containing a little lead) refined by cupellation.

The *uses of lead* are too familiar to require especial notice; this metal should never be employed for culinary utensils, since, in contact with air, and even weak acids, it is easily dissolved; the injurious properties of some kinds of cider are said to be due to their having been kept in leaden vats.

It would be well if this metal were never employed for water-cisterns (or even for water-pipes), since there is always some danger of dissolving a portion of the lead, and as it is a cumulative poison, the smallest quantity repeatedly taken into the system might seriously affect the health.

ALLOYS OF LEAD.

§ 322. Lead is capable of forming alloys with most other metals. A very small proportion entirely destroys the malleability of *gold*, *platinum*, and *silver*.

The alloys of lead and *tin* are harder and more fusible than the latter metal. The most fusible of these alloys is that containing 3 eqs. of tin to 1 eq. of lead, which fuses at 367° F. (186° C.), considerably below the fusing-point of either of these metals.

An alloy of equal weights of lead and tin constitutes *plumbers' solder*.

Certain inferior kinds of *pevter* are alloys of lead with 80 or 90 per cent. of tin.

The alloy used for lining the chests in which tea is imported contains 9 parts of lead and 1 of tin.¹

Type-metal is composed of 4 parts of lead and 1 part of antimony; a little bismuth is sometimes added.

¹ Crookes Witt has obtained alloys of lead and tin to which he assigns the formulæ Sn_2Pb , SnPb , and SnPb_2 . He also mentions alloys of copper and lead, having the composition Cu_2Pb , and CuPb .

Shots are made from an alloy of lead with from 0.3 to 0.8 per cent. of arsenic, which causes the drops of metal to assume a spherical form. The workmen judge when the necessary proportion of arsenic has been added by the form of the shots; too large a quantity of this metal renders them lenticular, whilst they are pyriform if enough arsenic be not added.

The fused metal is poured through a kind of sieve, which divides it into drops of various sizes, and allowed to fall from a considerable height into water. The sieve is lined with the matter which is scraped off the surface of fused lead at the commencement of oxidation. The shots are afterwards sorted, and polished in revolving boxes with a little plumbago.

ASSAY OF GALENA.—In order to determine the amount of lead contained in any specimen of this ore, 300 grs., in powder, are fused with 450 grs. of black flux (see p. 99) and 80 or 90 grs. of small iron nails, in a Hessian crucible, at a bright red heat. The sulphur is abstracted, partly by the iron, partly by the alkali of the flux, and a button of metallic lead is found at the bottom of the crucible; the latter is broken after the fusion, the button withdrawn, flattened under a hammer, to ascertain that it contains no iron nails, and weighed.

In this process, a certain quantity of lead passes into the slag, but the result is sufficiently accurate for most practical purposes.

The assay of ores of lead which are free from sulphur and arsenic may be effected by fusing them with carbonate of soda and charcoal.

SILVER.

Sym. Ag. Eq. 108.1. Sp. Gr. 10.474.

§ 323. This very beautiful and important metal is, like gold, pretty widely diffused, though in small quantities.¹ The description of its ores will be left for our subsequent consideration.

Preparation.—Standard silver is always alloyed with a certain quantity of copper, which we may separate by dissolving the alloy in dilute nitric acid, with the aid of heat, and adding solution of chloride of sodium as long as any precipitate is formed; the silver is thus precipitated as chloride, and the copper remains in solution. The chloride of silver is well washed by decantation as long as the washings give the slightest blue tinge with excess of ammonia; it is then dried, and reduced by either of the following methods: 1, By fusing in a Hessian crucible with an excess of carbonate of soda; 2, by fusing with 70 per cent. of chalk and 4 or 5 per cent. of charcoal; or, 3, by moistening with dilute hydrochloric acid, and placing in contact with a plate of zinc for some hours, then withdrawing the zinc, and washing the reduced metal by decantation with dilute hydrochloric acid (till the washings are no longer precipitated by ammonia and sulphide of ammonium), and subsequently with water.

The first two methods yield a compact globule of silver, the last gives the metal in spongy masses easily reduced to powder when dried.

A very ready method of obtaining pure silver from the solution of standard silver in nitric acid consists in evaporating the latter nearly to dryness, to expel excess of acid, diluting largely with water, and immersing a plate of copper (a clean penny answers the purpose), which precipitates the silver in a fine crystalline powder; when no more metal is precipitated, the copper is withdrawn, and

¹ In general, those ores which consist of oxides or salts are not so rich in silver as the sulphides: among the latter, iron-pyrites contains the least, and galena, zinc-blende, and copper-pyrites, the most silver.

the reduced silver washed by decantation till the washings are no longer tinged by ammonia.

This method is very useful for obtaining pure silver in order to prepare the nitrate, and, if carefully executed, it will be found that the metal is perfectly free from copper: Even should a little copper be found in it, digestion in ammonia will effect its removal.

Properties.—Pure silver has a dazzling white color, and is capable of a higher lustre than any other metal. From what has been stated above, it will be seen that it presents itself in different forms according to the method of preparation. When reduced by other metals at the ordinary temperature, it forms spongy masses, composed of crystalline grains which may easily be welded together. When precipitated from its solutions by reducing agents, it either forms a gray spongy mass, or a beautiful silvery coating upon the sides of the vessel. When obtained by sharply heating one of its salts, it presents a most beautiful dull white appearance; in any of these forms, however, it is recognized by the resplendent lustre which it acquires when burnished.

The specific gravity of silver is 10.4743; by hammering, however, it may be increased to 10.542.

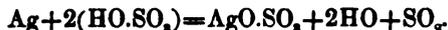
Silver is harder than gold, but not so hard as copper; it is more malleable and ductile than any other metal, except gold, being capable of extension into leaves of 0.00001 inch in thickness, and of being drawn out into the very finest wires. It surpasses gold in tenacity, but is inferior to iron, copper, and platinum; a silver wire, $\frac{1}{16}$ inch in diameter, will sustain a weight of 250 lbs. Silver fuses at a bright red heat, approaching to whiteness, and may be volatilized to some extent at very high temperatures, especially in a current of air or other gas; it volatilizes rapidly when heated in the oxyhydrogen blowpipe-flame, in the focus of a burning-glass, or between the charcoal points of a powerful galvanic battery.

Silver may be crystallized from a state of fusion, in cubes or octohedra.

Fused silver is capable of absorbing mechanically 22 volumes of oxygen, which is evolved when the metal solidifies, producing the peculiar arborescence alluded to in the description of the process of cupellation. The presence of a small quantity of copper prevents this phenomenon.

Silver is not affected by dry or moist air; it is tarnished, however, in an atmosphere containing sulphuretted hydrogen, which it decomposes, becoming coated with a film of sulphide of silver, which may be easily removed by a little solution of cyanide of potassium. Silver does not decompose water at any temperature.

Dilute sulphuric acid does not act upon silver, the concentrated acid, with the aid of heat, dissolves it in the form of sulphate:—



Dilute hydrochloric acid does not attack silver, but hot concentrated hydrochloric acid converts it, especially if finely divided, to some extent, into chloride, which dissolves in the acid, and is precipitated on dilution; the action of this acid upon silver is, however, very slow.

Nitric acid dissolves silver very rapidly, binoxide of nitrogen being disengaged:—



Phosphoric acid attacks silver only in the dry way.

The caustic alkalis and their nitrates do not attack this metal at a red heat; silver crucibles are therefore often useful in the laboratory; they should not be heated over a powerful gas-burner, lest they be fused; the heat of a common spirit-lamp is generally sufficient.

When silver is kept in contact for a length of time with common salt in a state

of fusion, a considerable quantity of chloride of silver is produced; the sodium being oxidized by the air. Vessels of silver are also attacked when solutions of alkaline chlorides are boiled in them for a long time, air having access.

A solution of sulphate of sesquioxide of iron is capable of dissolving silver at a high temperature:—



when the solution cools, the silver is deposited in minute crystals, sulphate of sesquioxide of iron being reproduced.

When finely divided silver is heated with the higher oxides of copper, lead, and manganese, it reduces them to their lowest state of oxidation.

Silver is attacked slowly by chlorine, bromine, and iodine; it combines directly with sulphur, selenium, and phosphorus, and with many metals.

SILVER AND OXYGEN.

Suboxide	Ag_2O
Oxide	AgO
Binoxide	AgO_2

SUBOXIDE OF SILVER, Ag_2O .

§ 324. When citrate of silver is heated to the boiling-point of water in a current of hydrogen, half the oxygen of the base is abstracted, and citrate of suboxide of silver produced; this salt dissolves in water, forming a brown solution, from which potassa throws down a black precipitate of suboxide of silver.

This suboxide is very unstable, it is readily decomposed by heat; hydrochloric acid converts it into brown subchloride of silver; all other acids decompose it into oxide and metallic silver.

OXIDE OR PROTOXIDE OF SILVER.

AgO . Eq. 116.1.

Preparation.—This oxide is prepared by decomposing solution of nitrate of silver with an excess of potassa; a grayish-brown hydrate is precipitated, which, when well washed and dried, either *in vacuo* or at a temperature of 140°F . (60°C .) becomes anhydrous.

Properties.—Oxide of silver is a dark brown powder, which is slowly reduced by exposure to light; a moderate heat decomposes it into its elements.

This oxide is somewhat soluble in water; the solution has a feeble alkaline reaction to reddened litmus. Oxide of silver is a powerful base, and dissolves readily, even in weak acids, forming well-defined salts, which are neutral to test-papers. Since the greater number of these salts are neutral in constitution, easily purified, and decomposed by heat, leaving metallic silver, they are very frequently made use of for determining the atomic weights of their acids, a determination which is capable of great accuracy, from the high equivalent of silver.

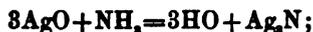
Oxide of silver dissolves readily in ammonia, if this reagent be added to the liquid in which the oxide is precipitated; but if the oxide of silver be washed and treated with ammonia, it forms a fulminating compound, which we shall revert to presently.

When heated with vitreous fluxes (glass, *e. g.*) oxide of silver combines with them, producing a yellow color.

Oxide of silver forms a compound with oxide of lead; when a solution of a salt of silver is mixed with excess of a lead-salt, and the mixture decomposed by potassa, a yellow precipitate is formed, containing $\text{AgO} \cdot 2\text{PbO}$.

FULMINATING SILVER.¹—The composition of fulminating silver is still uncertain.

It may be regarded either as a nitride of silver, Ag_2N (and this opinion is the most prevalent) produced according to the equation:—



as an amidide of silver, $\text{Ag}.\text{NH}_2$,



or lastly, as a compound of oxide of silver with ammonia; on either view its explosive powers would be explained by the instability of the compound, and the sudden evolution of a permanent gas.

Preparation.—Recently precipitated oxide of silver, still moist, is placed in contact with a little concentrated ammonia for some hours; a great part is dissolved, and a black compound remains, which must be thrown on a filter, and allowed to dry spontaneously; very small quantities should be prepared at once.

It may also be obtained by dissolving nitrate of silver in ammonia, and adding potassa in excess.

Properties.—Fulminating silver is sometimes crystalline; when dry, it explodes with the least touch; even under water it detonates if rubbed with a hard body, or heated. When acted on by acids, it yields silver-salts and salts of ammonia.

Fulminating silver is sometimes employed for making detonating balls.

§ 325. **NITRITE OF SILVER** ($\text{AgO}.\text{NO}_2$) is formed when nitrate of silver is heated moderately above its fusing point.

It is prepared by precipitating a solution of crude nitrite of potassa with nitrate of silver; it may be purified by dissolving in hot water and crystallizing. It forms fine yellow needles, sparingly soluble in cold water, but soluble in hot water; when the solution is long boiled, the nitrite of silver is partly reduced.

It is employed for the preparation of other nitrites by double decomposition.

NITRATE OF SILVER (*Lunar Caustic*).



Preparation.—Since this is the most important of the salts of silver, there exist several methods of preparing it.

I. The simplest of these consists in dissolving pure silver in dilute nitric acid, with the aid of heat, and evaporating to crystallization.

II. Nitrate of silver is, however, more frequently prepared from standard silver, which is alloyed with copper. Ordinary coin, for example, is dissolved in dilute nitric acid, the solution evaporated to dryness in a porcelain dish, and the residue heated nearly to redness; the nitrate of silver fuses without change, but the nitrate of copper is decomposed, evolving peroxide of nitrogen and oxygen, and leaving the black oxide of copper; a small portion of the mass is removed from time to time, dissolved in water, the solution filtered, and tested with excess of ammonia; when this reagent ceases to produce a blue color, the process is completed, and if the residue be treated with water, the solution will yield, on evaporation, crystals of pure nitrate of silver.

III. Another method of separating the oxide of copper from the nitric solution consists in displacing it by oxide of silver.

The nitric solution of the coin is evaporated to dryness, to expel excess of acid, and the residue is redissolved in water; $\frac{1}{2}$ of the solution is separated and precipitated with excess of potassa; the precipitated oxides of silver and copper

¹ This compound must not be confounded with *fulminate of silver*, which is a combination of oxide of silver with a peculiar acid, the fulminic (C_7O_2).

of fusion, a considerable quantity of chloride of silver is produced; the sodium being oxidized by the air. Vessels of silver are also attacked when solutions of alkaline chlorides are boiled in them for a long time, air having access.

A solution of sulphate of sesquioxide of iron is capable of dissolving silver at a high temperature:—



when the solution cools, the silver is deposited in minute crystals, sulphate of sesquioxide of iron being reproduced.

When finely divided silver is heated with the higher oxides of copper, lead, and manganese, it reduces them to their lowest state of oxidation.

Silver is attacked slowly by chlorine, bromine, and iodine; it combines directly with sulphur, selenium, and phosphorus, and with many metals.

SILVER AND OXYGEN.

Suboxide	Ag_2O
Oxide	AgO
Binoxide	AgO_2

SUBOXIDE OF SILVER, Ag_2O .

§ 324. When citrate of silver is heated to the boiling-point of water in a current of hydrogen, half the oxygen of the base is abstracted, and citrate of suboxide of silver produced; this salt dissolves in water, forming a brown solution, from which potassa throws down a black precipitate of suboxide of silver.

This suboxide is very unstable, it is readily decomposed by heat; hydrochloric acid converts it into brown subchloride of silver; all other acids decompose it into oxide and metallic silver.

OXIDE OR PROTOXIDE OF SILVER.

AgO . Eq. 116.1.

Preparation.—This oxide is prepared by decomposing solution of nitrate of silver with an excess of potassa; a grayish-brown hydrate is precipitated, which, when well washed and dried, either *in vacuo* or at a temperature of 140°F . (60°C .) becomes anhydrous.

Properties.—Oxide of silver is a dark brown powder, which is slowly reduced by exposure to light; a moderate heat decomposes it into its elements.

This oxide is somewhat soluble in water; the solution has a feeble alkaline reaction to reddened litmus. Oxide of silver is a powerful base, and dissolves readily, even in weak acids, forming well-defined salts, which are neutral to test-papers. Since the greater number of these salts are neutral in constitution, easily purified, and decomposed by heat, leaving metallic silver, they are very frequently made use of for determining the atomic weights of their acids, a determination which is capable of great accuracy, from the high equivalent of silver.

Oxide of silver dissolves readily in ammonia, if this reagent be added to the liquid in which the oxide is precipitated; but if the oxide of silver be washed and treated with ammonia, it forms a fulminating compound, which we shall revert to presently.

When heated with vitreous fluxes (glass, *e. g.*) oxide of silver combines with them, producing a yellow color.

Oxide of silver forms a compound with oxide of lead; when a solution of a salt of silver is mixed with excess of a lead-salt, and the mixture decomposed by potassa, a yellow precipitate is formed, containing $\text{AgO} \cdot 2\text{PbO}$.

FULMINATING SILVER.—The composition of fulminating silver is still uncertain.

It may be regarded either as a nitride of silver, Ag_3N (and this opinion is the most prevalent) produced according to the equation:—



as an amidide of silver, Ag.NH_2 ,



or lastly, as a compound of oxide of silver with ammonia; on either view its explosive powers would be explained by the instability of the compound, and the sudden evolution of a permanent gas.

Preparation.—Recently precipitated oxide of silver, still moist, is placed in contact with a little concentrated ammonia for some hours; a great part is dissolved, and a black compound remains, which must be thrown on a filter, and allowed to dry spontaneously; very small quantities should be prepared at once.

It may also be obtained by dissolving nitrate of silver in ammonia, and adding potassa in excess.

Properties.—Fulminating silver is sometimes crystalline; when dry, it explodes with the least touch; even under water it detonates if rubbed with a hard body, or heated. When acted on by acids, it yields silver-salts and salts of ammonia.

Fulminating silver is sometimes employed for making detonating balls.

§ 325. **NITRITE OF SILVER** (AgO.NO_2) is formed when nitrate of silver is heated moderately above its fusing point.

It is prepared by precipitating a solution of crude nitrite of potassa with nitrate of silver; it may be purified by dissolving in hot water and crystallizing. It forms fine yellow needles, sparingly soluble in cold water, but soluble in hot water; when the solution is long boiled, the nitrite of silver is partly reduced.

It is employed for the preparation of other nitrites by double decomposition.

NITRATE OF SILVER (*Lunar Caustic*).



Preparation.—Since this is the most important of the salts of silver, there exist several methods of preparing it.

I. The simplest of these consists in dissolving pure silver in dilute nitric acid, with the aid of heat, and evaporating to crystallization.

II. Nitrate of silver is, however, more frequently prepared from standard silver, which is alloyed with copper. Ordinary coin, for example, is dissolved in dilute nitric acid, the solution evaporated to dryness in a porcelain dish, and the residue heated nearly to redness; the nitrate of silver fuses without change, but the nitrate of copper is decomposed, evolving peroxide of nitrogen and oxygen, and leaving the black oxide of copper; a small portion of the mass is removed from time to time, dissolved in water, the solution filtered, and tested with excess of ammonia; when this reagent ceases to produce a blue color, the process is completed, and if the residue be treated with water, the solution will yield, on evaporation, crystals of pure nitrate of silver.

III. Another method of separating the oxide of copper from the nitric solution consists in displacing it by oxide of silver.

The nitric solution of the coin is evaporated to dryness, to expel excess of acid, and the residue is redissolved in water; $\frac{1}{2}$ of the solution is separated and precipitated with excess of potassa; the precipitated oxides of silver and copper

.. 3 This compound must not be confounded with *fulminate of silver*, which is a combination of oxide of silver with a peculiar acid, the fulminic (Cy_2O_2).

are washed with cold water, and boiled with the remaining $\frac{1}{3}$ of the solution, when the whole of the oxide of copper is precipitated, the oxide of silver taking its place.

IV. The nitric solution of the coin may also be diluted and precipitated by metallic copper, the precipitated silver being afterwards washed and dissolved in nitric acid.

V. It is frequently necessary to prepare nitrate of silver from the silver-residues in the laboratory; these should be entirely precipitated by hydrochloric acid, and the chloride well washed and reduced by one of the methods given for the preparation of pure silver (*see* p. 482).

The salt obtained by either of the above processes is purified by recrystallization, and dried on filter-paper in a dark place.

Lunar caustic of commerce is fused and cast into sticks.

Properties.—Nitrate of silver crystallizes in colorless square tables, which are anhydrous; when heated they fuse, and resolidify, on cooling, to a crystalline mass; a higher temperature expels part of their oxygen, leaving nitrite of silver, which is reduced to the metallic state when further heated.

Nitrate of silver dissolves in an equal weight of cold, and in much less boiling water; its aqueous solution is neutral. Alcohol also dissolves it to a considerable extent.

Light does not affect nitrate of silver unless organic matter be present, when the salt is reduced. Nitrate of silver corrodes the skin, producing black stains, which may be removed with iodide or cyanide of potassium; it also produces a black mark (probably metallic silver in a finely divided state) upon linen, and is hence employed in most permanent inks.

When boiled with finely divided metallic silver, the nitrate appears to yield compounds similar to those obtained by the analogous method from nitrate of lead.

Nitrate of silver, fused in a current of chlorine, yields chloride of silver, oxygen, and anhydrous nitric acid:—



Dry nitrate of silver absorbs ammoniacal gas, producing a compound of the formula $\text{AgO} \cdot \text{NO}_3 \cdot 3\text{NH}_3$, which is soluble in water, and easily decomposed by heat, ammonia being evolved.

If nitrate of silver be dissolved in excess of ammonia, and the solution evaporated, crystals are obtained, of the formula $\text{AgO} \cdot \text{NO}_3 \cdot 2\text{NH}_3$ (*ammonio-nitrate of silver*).

Uses.—Nitrate of silver is largely used in the laboratory for the precipitation of acids, and as a source of most of the other silver-salts. It is also employed both internally and externally in medicine. The small sticks used by the surgeon are often black externally, from the reduction of the silver by contact with metal or paper; sometimes, even, this black color extends throughout the mass, and may then be due to the presence of a little oxide of copper. It is also employed in photography.

HYPOSULPHITE OF SILVER, $\text{AgO} \cdot \text{S}_2\text{O}_3$.—This salt possesses some slight interest, because some of its compounds are produced when the alkaline hyposulphites are employed for fixing Daguerreotype pictures by removing the unaltered silver compound from the surface of the plate.

Hyposulphite of silver is obtained as a white precipitate by adding a dilute solution of hyposulphite of potassa to a slight excess of a dilute solution of nitrate of silver; the precipitate is very slightly soluble in cold water, and becomes black on exposure to light, being decomposed into sulphide of silver and sulphuric acid; it forms compounds with other hyposulphites, which possess greater stability.

The affinity of oxide of silver for hyposulphurous acid is so great, that it is capable of decomposing the alkaline hyposulphites, separating half of their bases, and forming soluble double hyposulphites, which are characterized by their remarkably sweet taste. These double hyposulphites may also be obtained by dissolving chloride of silver in the alkaline hyposulphites, and precipitating the double-salts by alcohol.

SULPHATE OF SILVER, AgO.SO_3 .—The sulphate may be prepared, either by precipitating a concentrated solution of nitrate of silver by sulphate of soda, or by dissolving silver in concentrated sulphuric acid, when the sulphate is deposited on cooling.

Sulphate of silver crystallizes in brilliant colorless prisms, which are decomposed only at a high temperature; it is sparingly soluble in cold water, but more so in hot water; it dissolves to a greater extent in concentrated sulphuric acid, and is precipitated on dilution.

Sulphate of silver dissolves in hot ammonia; the solution, on cooling, deposits crystals of the formula $\text{AgO.SO}_3.2\text{NH}_3$.

When calcined with carbon, sulphate of silver yields a mixture of metal and sulphide.

Carbonate of Silver (AgO.CO_2) is obtained by double decomposition. It is white, insoluble, and easily decomposed by heat.

BINOXIDE OR PEROXIDE OF SILVER, AgO_2 .

When a very dilute solution of nitrate of silver is decomposed by the galvanic current, dark gray lustrous needles of binoxide of silver are deposited around the positive pole.

Binoxide of silver is insoluble in water, and is decomposed by a temperature exceeding the boiling-point. It is an indifferent oxide, and therefore evolves oxygen when treated with oxygen-acids, and chlorine with hydrochloric acid, salts of silver being produced. When treated with ammonia, the hydrogen of the latter reduces the binoxide to (prot-) oxide, nitrogen being disengaged.

CHLORIDE OF SILVER, AgCl .

§ 326. The chloride of silver is found in nature crystallized in cubes (*horn-silver*); it is purely white, lustrous, and translucent, becoming violet or brown by exposure to light.

Chloride of silver may be obtained artificially by precipitating a solution of nitrate of silver with hydrochloric acid or a soluble chloride, stirring well, and washing the precipitate by decantation. Thus obtained it forms a white precipitate, which accumulates into curdy masses when stirred, especially if a little free nitric acid be present.

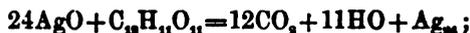
When exposed to light it becomes violet, and ultimately black; diffused daylight effects this slowly, but in sunlight the change takes place very speedily. The alteration of chloride of silver by exposure to light is said to be due to a disengagement of chlorine, and a reduction of the chloride to a subchloride, Ag_2Cl , for it does not take place in an atmosphere of chlorine, or under nitric acid, and if it be exposed in a moist state to the action of sunlight in a stoppered bottle, a strong smell of chlorine is perceived after 24 hours.

Chloride of silver, when heated, becomes gradually darker in color, and fuses at 500°F . (260°C .) into a brown oily liquid, which solidifies, on cooling, to a mass much resembling horn in external characters, and hence termed by the ancients *horn-silver*. Fused chloride of silver volatilizes to a slight extent when further heated; it cannot be decomposed by heat.

Iron crucibles are speedily penetrated by chloride of silver in a state of

This chloride is completely insoluble in water, and in nitric acid. Boiling concentrated hydrochloric acid dissolves it to a slight extent, and deposits it in octohedra when evaporated; the chloride of silver may also be precipitated from the solution by water. Concentrated sulphuric acid decomposes it slowly.

Caustic potassa and soda decompose chloride of silver at the temperature of ebullition, forming alkaline chlorides and oxide of silver; if a little sugar be added in this experiment, its carbon will be oxidized at the expense of the oxide of silver, carbonate of potassa being formed, and the silver reduced to the metallic state:—



Cane-sugar

this method is sometimes employed for the reduction of chloride of silver.

It is also reduced when fused with the alkaline and earthy carbonates:—



Chloride of silver is very commonly reduced by fusing with chalk and charcoal, which latter would tend to facilitate the decomposition by appropriating the oxygen of the lime:—



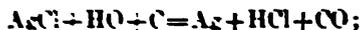
Ammonia readily dissolves chloride of silver, forming a colorless solution which deposits minute crystals of the chloride when evaporated, either spontaneously or with the aid of heat. If very concentrated ammonia be employed, the solution deposits a compound of chloride of silver with ammonia.

Chloride of silver absorbs $1\frac{1}{2}$ eq. of dry ammoniacal gas, with evolution of heat, producing a compound which gradually gives up its ammonia spontaneously, and with rapidity when very gently heated, so that it produces a sensation of great cold when placed upon the skin. It will be remembered that this compound is used for the preparation of liquefied ammonia.

Boiling solutions of the chlorides of potassium, sodium, barium, strontium, and calcium, are capable of dissolving chloride of silver, forming crystallizable double compounds which are decomposed even by water, but much more readily by concentrated nitric acid.

Chloride of silver dissolves also in solution of cyanide of potassium, forming a crystallizable double compound.*

Pure carbon is not capable of decomposing chloride of silver unless water be present, when hydrochloric acid and carbonic oxide are formed:—



common charcoal, therefore, is capable of reducing the chloride at a high temperature.

Iron and zinc decompose chloride of silver, even at the ordinary temperature, especially in presence of free hydrochloric acid, when the nascent hydrogen is probably the reducing agent.

Copper, tin, and lead, reduce chloride of silver in the dry way.

Mercury partially decomposes it, forming an amalgam of silver.

The property possessed by chloride of silver of blackening by exposure to light, is turned to advantage for the production of photographic pictures; the paper is washed, in a dark room, first with a silver-solution, and subsequently with chloride of sodium, which produces a film of chloride of silver; the paper is placed in a camera and the lights of the picture have sufficiently changed the chloride of silver, and the object is then fixed by washing in a darkened

* Some have been of opinion that chloride of silver is soluble to a considerable extent in solution of nitric acid, forming $\text{Ag}(\text{NO}_3)_2$, and may be obtained in crystals from such a solution.

The roasted ore is now ground in mills to a very fine powder, and introduced into strong casks made to revolve around a horizontal axis; in these casks the ore is agitated for an hour with water and a quantity of clean iron. The finely divided chloride of silver is reduced to the state of metal, the iron being converted into chloride; probably the presence of the common salt in solution assists this effect by dissolving the chloride of silver, and thus presenting it to the iron in a finely divided condition. The copper and lead are also reduced by the iron.

The charge for each of the revolving casks is generally about 1120 pounds of roasted ore, 83 gallons of water, and 112 pounds of fragments of iron. 560 pounds of mercury are then introduced into each cask, and the turning repeated for about eighteen hours. The silver, lead, and copper are dissolved by the mercury, forming an amalgam, which is accumulated by filling the casks with water, and again turning for some time, and afterwards drawn off.

This amalgam is strained through strong linen cloths, which separate the excess of mercury, leaving upon the strainer a solid amalgam containing about 82.85 per cent. of mercury.

The mercury is separated either by distilling the amalgam in iron cylinders provided with condensing-tubes dipping into water, or by placing it in shallow iron trays arranged one above the other, and covered with an iron dome standing over water; the dome is heated to redness, when the mercury rises in vapor from the trays, and condenses in the water.

The residual metal contains usually about 70 per cent. of silver, and 28 of copper, with traces of lead, nickel, arsenic, antimony, and mercury. It is refined by cupellation.

The silver obtained by cupelling lead on the large scale (as described at p. 480) is refined by a second cupellation on a smaller scale, which is continued until the surface of the fused metal remains perfectly bright.

In the American process of amalgamation the roasting is omitted, from the scarcity of fuel, and the silver is converted into chloride, by mixing the ore in a very finely divided state with chloride of sodium and roasted copper-pyrites (sesquioxide of iron and sulphate of copper), together with a sufficient quantity of water. The chloride of sodium and sulphate of copper suffer mutual decomposition, yielding sulphate of soda and chloride of copper, which acts upon the sulphide of silver in the ore, producing sulphide of copper and chloride of silver.¹ If the chloride of copper be in excess, a quantity of lime is added, in order to decompose it, lest a loss of mercury should be occasioned by its conversion into subchloride at the expense of the chloride of copper.

Mercury is now added to the mass, in the proportion of 6 or 8 parts for every part of silver to be extracted; the chloride of silver, dissolved in the solution of chloride of sodium, is reduced by the mercury, part of which is converted into subchloride, while the remainder dissolves the silver.

The amalgam is then treated as described in the former process.

In order to extract the silver from very poor ores, they are fused with iron-pyrites, and the argentiferous sulphide of iron thus obtained is first roasted, and then smelted together with lead-ores, when argentiferous lead is obtained, from which the silver is separated as usual.

In some parts of Mexico, the following methods are substituted for the amalgamation process:—

I. The ores are roasted with common salt, the resulting chloride of silver extracted from the mass by means of a solution of common salt, and the silver precipitated by metallic copper.

II. The sulphides are converted into sulphates by roasting, the mass treated with water, and the solution precipitated by copper.

¹ According to Karsten, subchloride of copper is formed and sulphur separated in the free state.

have been obtained directly, the compounds AgC and Ag_2C , have been produced by igniting, respectively, the cuminate and the maleate of silver.

These carbides are black, insoluble, and infusible; when heated in air, they smoulder, and leave a residue of metallic silver.

The alloys of silver will be described in the technical history of the metal.

METALLURGY OF SILVER.

§ 327. This metal occurs in a native state, crystallized in cubes, or forms derived therefrom; native silver is generally alloyed with other metals, especially with gold, arsenic, and antimony, and is often disseminated through galena and copper-ores.

The greater part of the silver found in nature is in the state of sulphide (*brittle silver-ore*), as we have more fully explained in another place.

It has also been mentioned that silver sometimes occurs in the form of chloride (*korn-silver*).

Carbonate of silver has also been found in the mineral kingdom.

The ores, from which the metal is chiefly extracted, are the sulphide, the antimonial sulphide, the native alloy of silver and antimony, and the chloride of silver.

EXTRACTION OF SILVER.—The processes for the extraction of silver from its ores may be conveniently divided into—1. Those in which the silver is obtained as a by-product, the chief object being to obtain another metal with which it is associated; and, 2. Those in which the extraction of silver is the main object of the process.

Those methods which belong to the first class are involved in the treatment of argentiferous lead and copper-ores; the former has been already noticed in the history of these metals.

When copper-ores contain a sufficient amount of silver to pay for extraction, they are smelted as usual, when an argentiferous copper is obtained; this is fused with three parts of lead, the resulting alloy cast into disks, which are subjected to liquation, *i. e.* placed upon a hearth and gradually heated, so that the greater part of the lead containing the silver may fuse and flow off, leaving a porous mass of copper, alloyed with lead and a very small quantity of silver. The argentiferous lead is then subjected to cupellation.

When the extraction of the silver from its ores, properly so called, is to be effected, the process of amalgamation is brought into use, which depends upon the affinity of silver for mercury.

There are two processes of amalgamating silver-ores, one of which is carried out in Europe (chiefly at Freiberg), the other principally in America, where fuel is less easily obtained.

Since these processes involve somewhat different reactions, we shall give a brief description of each separately.

The ore which is worked at Freiberg contains sulphide of silver, associated with much iron-pyrites, with other metallic sulphides and an earthy gangue.

A mixture of different specimens of ore is made, containing, at most, 0.0025 of silver, and 0.35 of iron-pyrites.

The ore is now mixed with one-tenth of common salt, and roasted in a reverberatory furnace; the sulphides of iron and copper are thus converted into sulphates, which are afterwards partly decomposed, sulphurous acid being evolved, and the oxides of iron and copper left; the sulphide of silver is also converted into sulphate by the sulphates of iron and copper; these three sulphates are decomposed by contact with chloride of sodium at a high temperature, sulphate of soda being formed, together with the chlorides of iron, copper, and silver.

The roasted ore is now ground in mills to a very fine powder, and introduced into strong casks made to revolve around a horizontal axis; in these casks the ore is agitated for an hour with water and a quantity of clean iron. The finely divided chloride of silver is reduced to the state of metal, the iron being converted into chloride; probably the presence of the common salt in solution assists this effect by dissolving the chloride of silver, and thus presenting it to the iron in a finely divided condition. The copper and lead are also reduced by the iron.

The charge for each of the revolving casks is generally about 1120 pounds of roasted ore, 83 gallons of water, and 112 pounds of fragments of iron. 560 pounds of mercury are then introduced into each cask, and the turning repeated for about eighteen hours. The silver, lead, and copper are dissolved by the mercury, forming an amalgam, which is accumulated by filling the casks with water, and again turning for some time, and afterwards drawn off.

This amalgam is strained through strong linen cloths, which separate the excess of mercury, leaving upon the strainer a solid amalgam containing about 82.35 per cent. of mercury.

The mercury is separated either by distilling the amalgam in iron cylinders provided with condensing-tubes dipping into water, or by placing it in shallow iron trays arranged one above the other, and covered with an iron dome standing over water; the dome is heated to redness, when the mercury rises in vapor from the trays, and condenses in the water.

The residual metal contains usually about 70 per cent. of silver, and 28 of copper, with traces of lead, nickel, arsenic, antimony, and mercury. It is refined by cupellation.

The silver obtained by cupelling lead on the large scale (as described at p. 480) is refined by a second cupellation on a smaller scale, which is continued until the surface of the fused metal remains perfectly bright.

In the American process of amalgamation the roasting is omitted, from the scarcity of fuel, and the silver is converted into chloride, by mixing the ore in a very finely divided state with chloride of sodium and roasted copper-pyrites (sesquioxide of iron and sulphate of copper), together with a sufficient quantity of water. The chloride of sodium and sulphate of copper suffer mutual decomposition, yielding sulphate of soda and chloride of copper, which acts upon the sulphide of silver in the ore, producing sulphide of copper and chloride of silver.¹ If the chloride of copper be in excess, a quantity of lime is added, in order to decompose it, lest a loss of mercury should be occasioned by its conversion into subchloride at the expense of the chloride of copper.

Mercury is now added to the mass, in the proportion of 6 or 8 parts for every part of silver to be extracted; the chloride of silver, dissolved in the solution of chloride of sodium, is reduced by the mercury, part of which is converted into subchloride, while the remainder dissolves the silver.

The amalgam is then treated as described in the former process.

In order to extract the silver from very poor ores, they are fused with iron-pyrites, and the argentiferous sulphide of iron thus obtained is first roasted, and then smelted together with lead-ores, when argentiferous lead is obtained, from which the silver is separated as usual.

In some parts of Mexico, the following methods are substituted for the amalgamation process:—

I. The ores are roasted with common salt, the resulting chloride of silver extracted from the mass by means of a solution of common salt, and the silver precipitated by metallic copper.

II. The sulphides are converted into sulphates by roasting, the mass treated with water, and the solution precipitated by copper.

¹ According to Karsten, subchloride of copper is formed and sulphur separated in the free state.

§ 328. **TECHNICAL HISTORY OF SILVER.**—The beauty of this metal, and its property of resisting the action of air and of weak acids, render it particularly valuable for the fabrication of ornaments and of domestic utensils.

We have already adverted to the use of some silver-compounds in medicine; the nitrate is the chief form in which this metal is employed; it has been remarked, in patients under treatment with this remedy, that exposure to light causes their skin to assume a purple color (from reduction of silver?). The oxide and chloride of silver are also occasionally employed; the solution termed "*liquor argenti auriatico-ammoniati*" is prepared by dissolving the chloride in ammonia, and partially neutralizing the latter with hydrochloric acid.

Pure silver is far too soft for any useful purpose; it is therefore usually alloyed with a certain quantity of copper. These two metals will combine, when fused together, in all proportions. The alloys thus formed are less malleable, harder, and more elastic than silver itself; they are white, unless they contain a considerable quantity of copper. The color of these alloys is generally improved at the surface by heating in air and immersing the metal in dilute sulphuric acid, which dissolves out the oxide of copper, leaving a superficial film of nearly pure silver.

The density of the alloys of copper and silver is rather higher than would be inferred from the respective densities of the two metals. When these alloys are fused and allowed to cool slowly, the metals separate to some extent, in consequence of the difference in their fusing points, and the cooled mass is therefore not homogeneous. If more than $\frac{1}{4}$ of copper be present, the alloy oxidizes when exposed to air (and its use for culinary purposes would therefore be attended with danger). When heated in air, the copper is gradually separated as oxide, the remaining alloy becoming richer in silver. The greater part of the copper may also be separated as sulphide, by heating the alloy with a quantity of sulphur insufficient to combine with the whole.

The alloy used in the silver coinage of England, and for most articles of domestic use, contains 11.1 parts of silver and 0.9 parts of copper.

The older specimens of standard silver, dating from a period before the introduction of the method of parting with sulphuric acid (see p. 399), contain a small quantity of gold, which is left behind as a dark purple powder on boiling the alloy with nitric acid.

Gold and silver may also be made to unite in all proportions, but the metals separate to some extent when the fused alloy is allowed to cool slowly. The density of the alloys of gold and silver is nearly what would be predicted. They are more fusible than gold, and are superior in hardness and elasticity to either of their constituent metals. Alloys of gold and silver are frequently employed for ornamental purposes.

In order to confer the beauty of silver upon articles of inferior cost, the base metals are often coated with silver by different processes, the most interesting of which we proceed to mention.

Plating, properly so called, consists in covering plates of copper with silver; to effect this, the surface of the copper is well cleaned, and washed over with a solution of nitrate of silver, which deposits a thin film of that metal upon its surface; a plate of silver, rather larger than the copper, is then applied to the latter, and its edges fixed down over those of the copper; the two are then heated to dull redness and passed between rollers.

Electroplating is effected by depositing a film of silver upon the surface of the article, by means of the galvanic battery, from a solution of cyanide of silver in cyanide of potassium: an outline of the process will be found in the section upon *gilding*, p. 414.

The *silvering upon glass*, which has of late years acquired considerable importance as an ornamental art, is effected by reducing the silver from a solution

by means of essential oils (or grape-sugar), the carbon and hydrogen of which readily abstract the oxygen from the oxide of silver, and cause the precipitation of the metal.

A solution of nitrate of silver is mixed with carbonate of ammonia and a little ammonia, and with a considerable quantity of alcohol; to this mixture are added solutions of oil of cassia and oil of cloves in alcohol; the glass to be silvered, having been thoroughly freed from grease, the liquid is heated in it to about 104° F. (40° C.), for two or three hours; the deposit is then formed upon the sides, and is washed, dried, and varnished.

For the analysis of alloys of silver, we refer to Quantitative Analysis, Special Methods.

Analysis of Ores of Silver.—The amount of silver in the ordinary ores, where it is associated with lead, copper, and sulphur, can scarcely be determined by the wet process.

Such ores are usually assayed by reducing the copper or lead to the metallic state (see pp. 389 and 482) and submitting the button to cupellation (see p. 401).

In principle, the assay of silver ores, therefore, is very similar to that of auriferous ores (see p. 402).

TANTALUM OR COLUMBIUM, NIOBIUM, PELOPHIUM, AND ILMENIUM.

§ 329. These very rare metals have been extracted from certain minerals known as *tantalites* and *ytro-tantalites*.

TANTALUM (Ta) is obtained by decomposing the chloride, at a red heat, with ammonia. It is a black, infusible powder, which assumes a metallic lustre when burnished. Heated in air, it burns, and is converted into tantalic acid.

Two oxides of tantalum exist; the (prot-) oxide, TaO, and tantalic acid, Ta₂O₅.

The oxide is obtained by reducing tantalic acid in a crucible lined with charcoal. It is a very hard, gray, indifferent substance, insoluble in acids.

Tantalic acid may be prepared by decomposing the sesquichloride of tantalum with water containing a little ammonia; it is a white, infusible substance, which becomes yellow when heated; tantalic acid dissolves in hydrochloric and hydrofluoric acids. Hydrated tantalic acid reddens litmus, and is soluble in potassa. Its salts are called *tantalates*.

Sesquichloride of tantalum (Ta₂Cl₇) is obtained in yellow prisms, by heating a mixture of tantalic acid and carbon in a current of chlorine. It is fusible and volatile.

Sesquisulphide of tantalum (Ta₂S₇) forms a gray powder with metallic lustre, obtained by heating tantalic acid in hydrosulphuric acid.

NIOBIUM (Nb) is obtained in a similar manner to tantalum. It is a black powder, which is converted into niobic acid when heated in air; it is insoluble in nitric acid and in *aqua regia*, but may be dissolved by a mixture of nitric and hydrofluoric acids.

Niobic acid (NbO₅?) may be obtained by decomposing the (ter?) chloride of niobium with water; it is a white powder, slightly soluble in hydrochloric acid; when fused with alkaline carbonates, it yields the alkaline *niobates*.

Chloride of niobium is prepared like sesquichloride of tantalum; and is volatile.

Sulphide of niobium is a black, crystalline substance, prepared by heating niobate of soda in a current of hydrosulphuric acid.

PELOPIUM (Pe) is prepared like the preceding metals, and much resembles tantalum.

Pelopic acid (PeO_3 ?) is prepared by decomposing the chlorine compound with water; it is very similar to tantalic acid, and is more soluble in hydrochloric acid than niobic acid. Its salts are termed *pelopiates*.

Chloride and *sulphide of pelopium* resemble the corresponding compounds of niobium, and are obtained in a similar manner.

ILMENIUM¹ has been found by Hermann, in place of tantalum, in the yttrantalite of Siberia; it is described as very similar to the preceding metals.

The hydrate of *ilmenic acid* is insoluble in hydrochloric acid.

Extraction of tantalum, niobium, and pelopium, from tantalites and yttrantalites.—These minerals contain tantalic, niobic, pelopic, and tungstic acids, in combination with lime, oxide of iron, oxide of uranium, and yttria. The following is the method employed by Berzelius for extracting the tantalic, niobic, and pelopic acids.

One part of the finely divided mineral is fused, in a platinum crucible, with 6 or 8 parts of bisulphate of potassa. The mass is powdered, and the soluble sulphates extracted by repeatedly boiling with water; the residue which contains the tantalic, niobic, and pelopic acids, is digested with sulphide of ammonium, which dissolves any tungstic and stannic acids, and converts the iron into sulphide. The residue is washed, and boiled with concentrated hydrochloric acid till it becomes white; in order to free it from silica, it is dissolved in hydrofluoric acid, the solution mixed with sulphuric acid, evaporated to dryness, and ignited as long as it loses weight, when all the silica is expelled as terfluoride of silica. The three acids contained in the mixture are separated by a laborious method founded upon the different volatility of the corresponding chlorides.

§ 330. In the following table, the chief physical properties of the metals in common use are expressed in such a manner as readily to admit of comparison.

Their *tenacity* is represented by the greatest weight which can be supported by a wire of $\frac{1}{8}$ inch in diameter; their *malleability*, *ductility*, and *fusibility* are indicated, in each case, by a number denoting its rank in the series; thus, the numbers, 1, 1, and 6, affixed to gold, show this metal to be the most malleable and ductile, and, with two exceptions, the least fusible.

Name.	Sp. gr.	Tenacity.	Malleability.	Ductility.	Fusibility.
Iron	7.7	705	8	4	7
Zinc	6.9	26	7	6	3
Copper	8.8	385	3	5	5
Gold	19.3	191	1	1	6
Platinum	21.0	361	5	3	8
Tin	7.3	47	4	7	1
Lead	11.5	20	6	8	2
Silver	10.5	250	2	2	4

¹ The existence of this metal has been denied by Rose.

ANALYTICAL CHEMISTRY.

QUALITATIVE ANALYSIS.

INTRODUCTION.

§ 881. THE term *analysis* implies the resolution of compound bodies into their components, and is distinguished as *proximate* or *ultimate* analysis, according as the substance under examination is resolved into its proximate constituents, or into its elements; thus, the proximate analysis of sulphate of potassa consists in the resolution of this salt into sulphuric acid and potassa, which are its proximate constituents; whereas, it would be the object of an ultimate analysis to decompose it into sulphur, oxygen, and potassium, which, since they are elements, are the limits beyond which analysis cannot proceed.

Hence, the importance of this branch of our subject will be apparent to all; in fact, analysis may be esteemed the basis of all chemical science; and, indeed, this branch of knowledge is sometimes defined as that which teaches the composition of all kinds of matter; and analysis, as above explained, is the operation by which the composition is ascertained.

The separation of the constituents of compound bodies is effected by converting either the constituent to be separated, or that other portion of the compound from which we intend to separate it, into a form different from that which it originally possessed; thus, in the analysis of the inferior oxides of nitrogen, the oxygen is separated by metallic copper, with which it enters into combination, and the *gas* is thus separated in the form of a *solid* (oxide of copper); again, oxygen may be separated from the oxide of copper, in the analysis of this substance, by means of hydrogen, which, at a high temperature, converts the oxygen into steam, thus removing it, in a *gaseous* form, from its *solid* combination.

Precipitation, however, is most frequently employed for the separation of substances from each other. This operation consists in the conversion of one constituent part of a liquid into a solid form, when it may be separated by mechanical means; this may be effected either by changing the chemical nature of the constituent to be separated, or that of the liquid in which this constituent is dissolved; the first method is illustrated by the separation of baryta from the nitrate by the addition of sulphuric acid, which converts the baryta into an insoluble sulphate, whilst the second mode of precipitation is had recourse to in the separation of oxide of copper from the sulphate by the addition of potassa, which converts the sulphuric acid (in which the oxide of copper was dissolved) into sulphate of potassa, and a solution of this salt being incapable of dissolving the oxide of copper, this latter is precipitated.

From these examples, it will be seen that a knowledge of the operation of *affinities* under various conditions is of very great service to the analytical chemist, who should also be acquainted with the chemical relations of the most common acids, bases, and salts, which he will apply in the course of analysis, and it is

therefore almost indispensable to acquire a pretty good knowledge of general chemistry before entering upon the study of analysis; and although one who has not thus qualified himself may attain to great readiness in the application of this instrument of investigation, and great familiarity with the systematic course marked out for him, he will find that every case not provided for in the general rules will be fraught with difficulties which are insuperable to one whose whole knowledge consists only in a mechanical familiarity with a certain routine of processes and manipulations, and is not founded, as it should be, upon a correct acquaintance with the properties of the elementary forms of matter and of their various combinations.

Qualitative analysis shows us merely the nature of the component parts of a substance, whilst the determination of their quantity is the object of a *quantitative analysis*; of course, a quantitative analysis must be preceded by a qualitative; we must know what the ingredients are, before we attempt to ascertain their amount.

The method to be pursued in the study of qualitative analysis is, obviously, to acquaint ourselves, first, with the properties of those substances the detection and separation of which we have in view; then to ascertain how far these properties are modified, when the various substances exist together in a compound or mixture; and lastly, to deduce from these observations methods of effecting their separation. And here we may remind the reader of the difference between *testing* and *analysis*; we test for any particular substance by eliciting some property peculiar to itself, such as a change of color or production of some peculiar odor, which would not afford us any assistance in the separation of such bodies, i. e. in the analysis of their combinations.

Great caution is obviously essential to successful analysis; it is well to bring the greatest amount of evidence to support the presence of any substance, by eliciting as many as possible of the properties of that substance; and we must, above all, beware of jumping to conclusions, as it is termed, by accepting a chain of evidence in which a few links are wanting, because we imagine that the improbability of our mistaking the body in question is greater than the confirmation which the presence of these links would afford. We must also, by dint of long practice in the analysis of bodies of known composition, learn to assign to each indication its own proper weight, and no more; otherwise, by exaggerating its value, we are in danger, either of inferring the presence of any substance from proof which is really insufficient, or of setting it down as absent upon the testimony of a reaction, the failure of which ought to be ascribed to some modifying cause with which we may be unacquainted.

Thus, too much reliance should not be placed upon the color and appearance of precipitates, which may be influenced by a great variety of causes; but we should rather learn to recognize them by their chemical relations, their solubility, insolubility, &c., which characters are generally as constant as the others are liable to change.

The chemical analyst, especially at the commencement of his studies, generally finds it advantageous to note down each step taken, with its result, and the conclusion drawn from it; such notes not only enable him to discover and retrieve any error into which he may have fallen, but, if preserved, are very useful for reference and comparison.

APPARATUS USED IN QUALITATIVE ANALYSIS.

§ 832. The apparatus requisite for the practice of qualitative analysis is very simple; the following list comprises all those instruments with which the student should provide himself at the commencement.

- Two or three dozen of *German test-tubes*, and stand with *draining pegs*; *brush* for cleaning the tubes.
 A *test-tube holder*. (Fig. 70.)
 A few *glass funnels* capable of containing from eight ounces to half an ounce.
 A selection of *Berlin dishes*, and of *Berlin crucibles* (Fig. 71) with covers.¹
 Small *flasks* of German glass, holding from four to eight ounces.
Glass rod and *tube* of various sizes.
 A *washing-bottle* containing about sixteen ounces. (Fig. 72.)
 A *spirit-lamp*. (Fig. 73.)
 A few German *beakers*, from one to sixteen ounces.
 A *pestle and mortar* of Berlin or of Wedgwood ware.
- Small *sand-tray*.
Watch-glasses.
Cork-borers (Fig. 74), round and triangular *files*, *scissors*.
Cork-rasp, *spatula*.
 A number of the best *corks*.
 A few lengths of small *vulcanised tubing*.
 Small *crucible-tongs*.
 A few *iron spoons*; *iron wire triangles* for supporting crucibles, &c.
 Black's *blowpipe*.
Platinum wire and foil.
 Small *retort-stand*.
 Good *filtering-paper*.
Blue and red litmus-papers.
Sulphuretted hydrogen apparatus. (Fig. 75.)

Fig. 70.

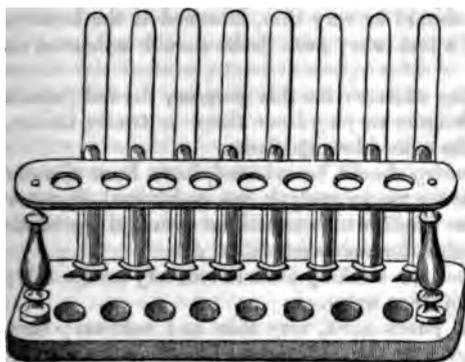


Fig. 74.

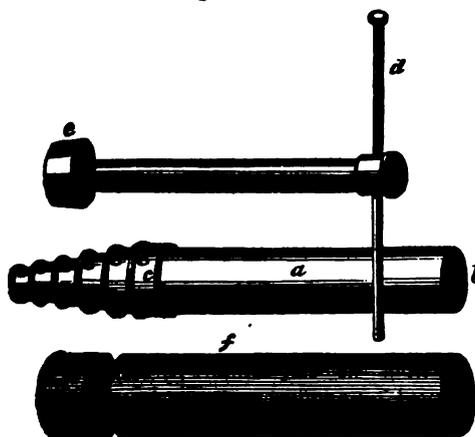


Fig. 71.



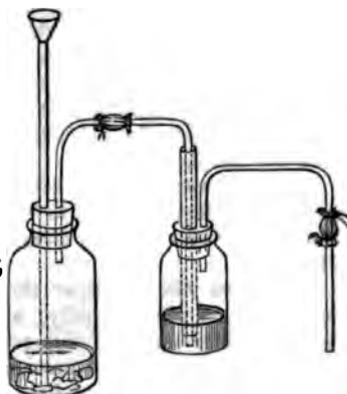
Fig. 73.



Fig. 72.



Fig. 75.



¹ Meissen ware may be substituted for these.

The particulars to be attended to in the selection of these different apparatus, as well as the precautions in their use, have been in great measure described already; we need therefore only subjoin here a few remarks, especially relating to the use of the apparatus in qualitative analysis.

The most convenient *test-tubes* will be found to be about six inches in length, and about three-fourths of an inch in diameter; they should be made of very thin German glass, and furnished with a smooth lip, but no spout. A few wider tubes will also be found useful for boiling liquids. The test-tubes should be thoroughly cleaned, after use, by brushing; they should then be rinsed with distilled water, and inverted upon the draining-pegs.

The *funnels* should be plain, not ribbed, and the sides should form, as nearly as possible, an angle of 45° with the stem.

The Berlin *crucibles* should be of uniform thickness, and provided with light covers; in capacity, they should vary from one to four fluidrachms, the latter size being the most useful.

Porcelain *dishes* for qualitative analysis should vary in size, from one pint to half an ounce; they should be nearly hemispherical in shape, and should have a spout to pour from; it is better to have them glazed within and without. These dishes are often required to stand the application of a red heat, and, in this respect, the Berlin ware is much preferable to any other.

The *flasks* employed in analysis should be very thin, flattened at the bottom, and provided with a lip like that of a test-tube; such flasks should be heated on a sand-bath.

Glass rod is very useful for making stirrers; for this purpose, the rod (which should be rather thin) is cut into lengths varying from three to twelve inches, the ends of which are rounded in the outer blowpipe-flame.

The characters by which *glass tubing* should be selected, have been already mentioned; the most convenient size for use in analysis has an internal diameter of about one-sixth of an inch; some English tube should be provided for bending, and a few lengths of German glass for reduction tubes, &c.

In a former page, we have described the *washing-bottle* in ordinary use (p. 92); the one here figured may be used with hot water.

The *beakers* should be without a punty-mark, very thin and uniform; they should be heated on a sand-bath, never by the bare flame.

A small *mortar* of Berlin porcelain, capable of containing about eight ounces, will be found most useful.

The *watch-glasses* should be made of thin, well-annealed glass; they will generally bear heating upon the sand-bath, but rarely over the flame.

The *crucible-tongs* in general use are made of iron, but it is very advantageous to have them tipped with platinum, although they become then very much more expensive. The ordinary iron tongs should not be employed for lifting dishes containing liquids likely to corrode the iron, and thus to become contaminated with this metal.

An iron *retort-stand* with three or four movable brass rings, from two to four inches in diameter, serves to support funnels, dishes, and crucibles; the latter should never be supported directly by the ring of the retort-stand, always upon a triangle.

Qualitative *filtering-paper* should be moderately strong, and should allow liquids to pass pretty rapidly; when boiling dilute hydrochloric acid is poured through a filter made of this paper, it should take up no alumina or earthy phosphate (which may be precipitated from the acid solution by excess of ammonia), nor any traces of lime (detected by adding ammonia in excess, and oxalate of ammonia, which would produce a white precipitate).

The blue and red *litmus-papers* should be made of opaque very thinly sized paper, not too strongly tinted.

The *sulphuretted hydrogen apparatus* consists of a generating bottle (capable of containing about twelve ounces) furnished with a funnel-tube for adding the acid, and with a tube bent at right angles, connected, by means of caoutchouc, with a second glass tube which conveys the gas to the bottom of a small bottle, containing a little water to free it from mechanically suspended impurities; from this wash-bottle, another tube proceeds, which is bent twice at right angles; to the disengaged extremity of this tube, there is attached, by a connector, a straight piece of tube, which serves to convey the gas into any solution through which we intend to pass it.

REAGENTS USED IN QUALITATIVE ANALYSIS.

§ 333. The reagents employed in qualitative analysis come next under consideration.

Reagents are the substances employed by the analyst in ascertaining the nature of a body under examination; they are usually divided into *general* and *special* reagents; the former designation is commonly applied to those substances which are used to separate bodies into different groups, and the latter, to those employed to distinguish the members of these groups from each other. We shall, however, give a wider sense to the term *general reagents*, and employ it to denote all those which are frequently used in analysis, whilst the *special reagents* are such as are only used to detect individual substances.

The general reagents are most conveniently arranged over the working-table within reach of the operator, whilst the special reagents may be placed in any other part of the laboratory.

In the following list, we have adopted this division into general and special reagents; and it may be remarked that comparatively small quantities of the special reagents are employed, unless otherwise mentioned.

GENERAL REAGENTS.

In solution.

- | | |
|---|--|
| 1. Concentrated sulphuric acid (HO.SO_3). | 13. Phosphate of soda (2NaO.HO.PO_2). |
| 2. Dilute " " " | 14. Ammonia (NH_4O). |
| 3. Concentrated hydrochloric acid (HCl) | 15. Sesquicarbonate of ammonia ($2\text{NH}_4\text{O.3CO}_2$). |
| 4. Dilute " " " | 16. Oxalate of ammonia ($\text{NH}_4\text{O.C}_2\text{O}_4$). |
| 5. Concentrated nitric acid (HO.NO_2) | 17. Chloride of ammonium (NH_4Cl). |
| 6. Dilute " " " | 18. Sulphide of ammonium (NH_4S). |
| 7. Acetic acid ($\text{HO.C}_2\text{H}_3\text{O}_2=\text{HO.A}$). | 19. Chloride of barium (BaCl). |
| 8. Tartaric acid ($2\text{HO.C}_4\text{H}_4\text{O}_6=2\text{HO.T}$). | 20. Lime (CaO.HO). |
| 9. Hydrosulphuric acid (HS). | 21. Sulphate of lime (CaO.SO_3). |
| 10. Potassa (KO.HO). | 22. Chloride of calcium (CaCl). |
| 11. Ferrocyanide of potassium ($\text{K}_2\text{Cy}_2\text{Fe}=\text{K}_2\text{Cy}$). | 23. Sesquichloride of iron (Fe_2Cl_3). |
| 12. Carbonate of soda (NaO.CO_2). | |

In the solid state.

- | | |
|---|--|
| 24. Nitrate of potassa (KO.NO_3). | 27. Carbonate of soda (NaO.CO_2). |
| 25. Carbonate of potassa and soda ($\text{KO.CO}_2+\text{NaO.CO}_2$). | 28. Biborate of soda (NaO.2BO_3). |
| 26. Cyanide of potassium ($\text{KC}_2\text{N}=\text{KCy}$). | 29. Hydrate of lime (CaO.HO). |

SPECIAL REAGENTS.

In solution.

- | | |
|--|--|
| 1. Sulphurous acid (SO_2). | 10. Sulphate of magnesia (MgO.SO_3). |
| 2. Oxalic acid ($\text{HO.C}_2\text{O}_3=\text{HO.O}$). | 11. Nitrate of cobalt (CoO.NO_3). |
| 3. Hydrofluosilicic acid (3HF.2SiF_3). | 12. Sulphate of manganese (MnO.SO_3). |
| 4. Sulphate of potassa (KO.SO_3). | 13. Acetate of lead (PbO.A). |
| 5. Bichromate of potassa (KO.2CrO_3). | 14. Sulphate of copper (CuO.SO_3). |
| 6. Acetate of potassa (KO.A) [<i>in considerable quantity</i>]. | 15. Chloride of mercury (HgCl). |
| 7. Ferricyanide of potassium ($\text{K}_3\text{Cy}_3\text{Fe}_2=\text{K}_3\text{Cfdy}$). | 16. Chloride of tin (SnCl). |
| 8. Sulphite of ammonia ($\text{NH}_4\text{O.SO}_3$) [<i>in considerable quantity</i>]. | 17. Bichloride of platinum (PtCl_2). |
| 9. Baryta (BaO.HO) [<i>in considerable quantity</i>]. | 18. Nitrate of silver (AgO.NO_3) [<i>in considerable quantity</i>]. |
| | 19. Alcohol ($\text{C}_2\text{H}_5\text{O}_2$). |
| | 20. Ether ($\text{C}_2\text{H}_5\text{O}$). |
| | 21. Solution of indigo ($\text{C}_{16}\text{H}_8\text{NO}_2$). |

In the solid state.

- | | |
|--|---|
| 22. Chlorate of potassa (KO.ClO_3). | 28. Binocide of manganese (MnO_2). |
| 23. Phosphate of soda and ammonia ($\text{NaO.NH}_4\text{O.HO.PO}_3$). | 29. Granulated zinc (Zn). |
| 24. Hydrate of baryta (BaO.HO). | 30. Copper foil or wire (Cu). |
| 25. Dry chloride of calcium (CaCl). | 31. Starch ($\text{C}_6\text{H}_{10}\text{O}_5$). |
| 26. Carrara marble (CaO.CO_3). | 32. Sulphur (S). |
| 27. Sulphate of iron (FeO.SO_3). | 33. Sulphide of iron (FeS). |

It is obvious that these reagents should all be perfectly pure, but since, in many cases, it is exceedingly difficult to procure the substances in a state of absolute purity, it is allowable to employ them, although slightly contaminated, provided that the impurities are known to the operator, and are not such as will interfere with the particular use of the reagent in question.

Since this subject possesses great practical importance, we shall now proceed to consider the particular impurities to which each reagent is liable, and the manner of testing for them; noticing, at the same time, the general use to which the reagent is applied, unless this has been referred to in a previous section.

GENERAL REAGENTS EMPLOYED IN SOLUTION.

Concentrated Sulphuric Acid.—The ordinary oil of vitriol sold by operative chemists is sufficient for most purposes; it should be colorless, and free from nitric acid, which may be ascertained by diluting it with an equal volume of water, allowing the mixture to become nearly cool, and adding a crystal of sulphate of iron; if the liquid be allowed to remain perfectly at rest for some minutes, a brown halo will form around the crystal if the least trace of nitric acid is present.

Perfectly pure (distilled) sulphuric acid is necessary, however, for some purposes; this should be tested especially for sulphate of lead, nitric acid, and arsenious acid.

The presence of sulphate of lead may be readily ascertained by mixing the acid with three or four times its volume of water, when this impurity would be thrown down as a white precipitate.

Nitric acid may be tested for as above.

Arsenious acid should be sought by *Marsh's test*, which will be described hereafter; this is not a common impurity of sulphuric acid at the present day.

Dilute sulphuric acid is prepared by mixing, in a beaker, one measure of the concentrated acid with six measures of water.

Sulphuric acid, in the concentrated state, is chiefly used for evolving sul-

phuretted hydrogen, and for decomposing certain salts, for which purposes it need not be absolutely pure. The dilute acid is generally used for precipitating lead, baryta, &c., and should therefore be free from all impurities.

Concentrated hydrochloric acid should have a specific gravity of about 1.20, and must be perfectly colorless. The impurities most likely to occur in concentrated hydrochloric acid are sulphate of soda, sulphurous acid, free chlorine, and chloride of iron, which latter usually imparts a yellow tint to the acid. The sulphate of soda may be detected by diluting the acid with four or five measures of water, and adding chloride of barium, when a white precipitate of sulphate of baryta will make its appearance. The presence of sulphurous acid may be ascertained by boiling the acid with a few drops of pure nitric acid, which converts the SO_2 into SO_3 , diluting with much water, and adding chloride of barium.

If the hydrochloric acid contains free chlorine, it will decolorize solution of indigo.

Iron may be tested for by adding an excess of ammonia to the acid, and then a drop of sulphide of ammonium, which will produce a greenish-black precipitate or tinge, due to sulphide of iron.

Pure hydrochloric acid should leave no residue when evaporated on platinum.

One measure of hydrochloric acid should be mixed with two measures of water, for the preparation of the dilute acid.

Hydrochloric acid is generally employed where a free mineral acid is required, the nature of which is a matter of indifference, since it is not liable to alter bodies by oxidation, like nitric acid, nor to form insoluble compounds, like sulphuric acid; thus it is very frequently employed as a solvent in analysis, and should therefore be absolutely pure.

Concentrated nitric acid used in analysis has a specific gravity of 1.48 to 1.50. It is liable to contain inferior oxides of nitrogen (NO , and NO_2), sulphates of potassa and soda, and chlorine.

The lower oxides of nitrogen impart a red or yellow color to the acid, and, for most purposes, are not objectionable.

The sulphates of potassa and soda may be detected by diluting largely with water, and testing with chloride of barium.

If the acid contains chlorine, it will give a white precipitate of chloride of silver, upon addition of solution of nitrate of silver.

Pure nitric acid should leave no residue on platinum.

Dilute nitric acid is a mixture of one measure of the concentrated acid with two measures of water.

Nitric acid is generally used as an oxidizing agent, and but rarely as a simple solvent; for the latter purpose the dilute acid is generally employed.

Acetic Acid.—The ordinary acetic acid of the druggists is sufficiently strong for most purposes. It should be tested for sulphuric acid with chloride of barium, and for sulphurous acid with the same reagent, after having been boiled with a little nitric acid, and diluted with water; pure acetic acid must not be discolored by hydrosulphuric acid, and should volatilize entirely when heated. Acetic acid is generally used in analysis, where a vegetable acid is required.

Tartaric acid of commerce is sufficiently pure for the purposes of analysis; it should be used in the form of a cold saturated solution, prepared by agitating the crystals with water, and allowing them to remain in contact with the latter till no more is dissolved; this solution decomposes after some days, depositing white flocks, which, however, do not interfere materially with the applications of the reagent.

Hydrosulphuric acid is merely a saturated aqueous solution of the washed gas; this reagent should be kept in bottles nearly filled with it, and well stopped, since it is rapidly oxidized by contact with air; it should be freshly prepared every two or three days. Hydrosulphuric acid is one of the most useful gene-

ral reagents, since, by precipitating sulphides of various colors, it enables us to recognize many metals with great facility.

Potassa is very difficult to obtain perfectly pure, and although, strictly speaking, none but pure potassa should be used in analysis, it is very far too costly for ordinary purposes, and we therefore generally content ourselves with such as contains but a small amount of impurity.

The ordinary impurities of solution of potassa are silica, alumina, carbonic acid, sulphuric acid, hydrochloric acid, and oxide of lead.¹

Silica may be detected in solution of potassa, by adding an excess of hydrochloric acid, evaporating to dryness, and heating the residue with dilute hydrochloric acid, when flakes of silica will remain insoluble; if alumina is present, it will be precipitated by ammonia from the hydrochloric solution filtered from the silica.

The carbonic acid will be indicated by the effervescence which takes place when the solution of potassa is mixed with excess of hydrochloric acid; a small quantity of carbonic acid is not objectionable in most of the applications of potassa.

The solution, mixed with excess of hydrochloric acid, may be tested for sulphuric acid with chloride of barium.

The presence of hydrochloric acid may be shown by acidulating with nitric acid, and testing with nitrate of silver.

Oxide of lead may be tested for with hydrosulphuric acid, which will furnish a black precipitate of sulphide of lead.

Good potassa should contain only small quantities of silica, alumina, sulphuric acid, and hydrochloric acid, should effervesce but slightly with acids, and should be free from oxide of lead.

The analyst should also have a small store of pure potassa (*alcohol-potassa*, as it is termed), for cases in which it is desirable to test for silica and alumina with great minuteness.

Potassa is chiefly used for dissolving certain metallic oxides (for example, alumina and oxide of zinc), and thus separating them from others which are insoluble in this alkali.

Ferrocyanide of Potassium.—This salt, as it is found in commerce, may be employed as a reagent; one part of the crystals is dissolved in ten parts of water. It is used as a special test for iron, copper, &c.

The *carbonate of soda* employed in analysis should be perfectly pure; it is liable to be contaminated with sulphuric acid, chlorine, silica, hydrate of soda, alumina, and lime. Its aqueous solution may be tested for sulphuric acid with chloride of barium, after addition of an excess of hydrochloric acid; for chlorine with nitrate of silver, after adding excess of nitric acid; for silica, by evaporating the solution, mixed with hydrochloric acid in excess, to dryness, and redissolving in dilute hydrochloric acid, when flakes of silica would be left behind; alumina may be precipitated from the acid solution thus obtained, by ammonia, and lime will then be indicated by oxalate of ammonia.

If sulphide of sodium be present, the aqueous solution will give a somewhat gray precipitate with acetate of lead, which should throw down white carbonate of lead only, if the specimen be perfectly pure.

In order to ascertain whether any hydrate of soda is present in a specimen of the carbonate, the aqueous solution of the latter is mixed with solution of chloride of barium, as long as any precipitate is produced; this precipitate of carbonate of baryta is rapidly filtered off, and a piece of reddened litmus-paper immersed in the filtrate; if the latter evince an alkaline reaction, it is a proof of the presence of hydrate of soda in the original solution.

¹ This last impurity is avoided if the potassa be kept in bottles of German glass, which contains no lead, instead of in those of ordinary flint-glass.

The solution of carbonate of soda for use in analysis is best prepared by dissolving the salt in so much warm water that the solution shall be saturated when cold.

Carbonate of soda is in frequent use for neutralizing acid solutions where it is desirable to avoid the introduction of ammonia, and for decomposing certain salts which are insoluble in water, and would be destroyed if dissolved in acids.

Phosphate of soda is met with in commerce of sufficient purity for analytical purposes; one part of the crystals may be dissolved in six parts of water.

Solution of phosphate of soda should be kept in bottles of German glass, since it acts upon common flint-glass, giving rise to an opaque precipitate of phosphate of lead.

Ammonia is one of the most important reagents in the laboratory; it is prepared of suitable strength by mixing the solution of ammonia of sp. gr. 0.87 with an equal volume of water. Solution of ammonia is very seldom impure; it may contain chloride of ammonium, carbonate of ammonia, and sometimes traces of lime; the chlorine may be detected by adding excess of nitric acid and nitrate of silver; the carbonic acid will produce a turbidity in solution of chloride of calcium, and the lime will be indicated by a white precipitate on addition of oxalate of ammonia. Pure ammonia should leave no residue on evaporation.

Ammonia is constantly employed to precipitate metallic oxides from their salts, and for neutralizing solutions previously to analysis; it is therefore highly important that it be perfectly pure.

Sesquicarbonate of ammonia, in solution, is prepared by agitating the commercial sesquicarbonate, broken into small fragments, with cold water, as long as any of the salt is dissolved.

The sesquicarbonate of ammonia is liable to contain bicarbonate, which constitutes the opaque white crust seen on the surface of the former salt after exposure to the air; it also sometimes contains a little oxide of iron, which will give a greenish-black tinge with sulphide of ammonium.

Sesquicarbonate of ammonia should leave no residue when heated on platinum. This reagent is chiefly used in the separation of tin, antimony, and arsenic, and in the precipitation of the alkaline earths.

Oxalate of ammonia is used as a special test for lime; a cold saturated solution may be prepared for this purpose, by agitating the crystals with water as long as any of the salt is dissolved.

Chloride of ammonium, as met with in commerce, is not sufficiently pure for analytical purposes, since it contains a considerable quantity of iron; one recrystallisation generally purifies it sufficiently. This salt should volatilize perfectly on platinum, and should not give any tinge of sulphide of iron upon addition of sulphide of ammonium.

Sulphide of ammonium is very extensively employed in analysis for separating certain classes of metallic oxides.

When freshly prepared, sulphide of ammonium is colorless, but after some time, it becomes yellow in consequence of an absorption of oxygen from the air; thus:—



Since this NH_4S_2 (bisulphide of ammonium) is frequently useful, and very rarely objectionable, it is better to employ the light yellow sulphide of ammonium as a reagent.

Sulphide of ammonium should not give any precipitate with solution of sulphate of magnesia, nor leave any fixed residue when evaporated on platinum; the yellow sulphide, when mixed with excess of hydrochloric acid, should give a perfectly white precipitate of sulphur.

Chloride of barium is liable to a very dangerous impurity, chloride of lead, which may be detected by the black tinge produced by hydrosulphuric acid; it

may be purified easily by recrystallization, or the lead may be precipitated by hydrosulphuric acid, the solution evaporated till the excess of this reagent has been expelled, and, after separating the precipitated sulphur by filtration, evaporated to crystallization. A cold saturated solution of chloride of barium is most convenient for ordinary use.

This reagent is largely employed in the detection of the acids; its purity from lead is therefore matter of importance.

Lime-water is very useful in the detection of carbonic acid; it is prepared by shaking freshly slaked lime with cold distilled water, allowing the excess of lime to subside, and decanting the clear liquor, which should be kept in well-stoppered bottles, since it is very liable to absorb carbonic acid from the air. Its alkaline reaction may serve to indicate its strength.

Sulphate of Lime.—The solution of this salt is prepared by boiling an excess of precipitated sulphate of lime with water, which dissolves very little of it, and filtering. It is used to distinguish between baryta and strontia.

Chloride of Calcium is largely used in the detection of the acids; its solution should be prepared by dissolving the crystals in three parts of water. The solution of chloride of calcium should not be precipitated by ammonia, which would throw down alumina, nor by sulphate of lime, which would indicate baryta and strontia.

Sesquichloride of iron should not have a powerful acid reaction, and should yield a permanent precipitate when stirred with a glass rod dipped in solution of ammonia; it should contain no (proto-) chloride of iron, which is indicated by the production of a blue precipitate on adding solution of ferricyanide of potassium to the highly diluted sesquichloride. The solution should be diluted till of a somewhat light sherry color; it is used in the detection of certain acids, especially of phosphoric acid.

GENERAL REAGENTS EMPLOYED IN THE SOLID FORM.

Nitrate of potassa of commerce should be purified by recrystallization. It is liable to contain sulphate of potassa and chloride of potassium; the presence of the former will be indicated by chloride of barium, that of the latter by nitrate of silver. The crystals should be powdered, and dried at a gentle heat.

Carbonate of Potassa and Soda.—This reagent consists of a mixture of equivalent weights of the two carbonates (about four parts of dried carbonate of potassa and three of dried carbonate of soda), and is much more fusible than either of the salts separately.

The mode of ascertaining the purity of carbonate of soda has been mentioned above; carbonate of potassa is liable to the same impurities.

It is highly important that this reagent be perfectly pure, since it is constantly employed in the analysis of insoluble substances, such as the natural silicates. This mixture may be advantageously prepared by incinerating the double tartrate of potassa and soda (*Rochelle salt*) in a platinum dish, till all the carbon has burnt off, which may be hastened by stirring.

Cyanide of potassium has already been mentioned under the head of blowpipe-reagents (p. 107); it should be perfectly white, and must be kept in bottles which are well closed with sound corks, since glass stoppers are very liable to become fixed in the bottles.

We have already mentioned (p. 107) the use of cyanide of potassium as a reducing agent; it is sometimes employed, also, in the state of solution, which should be prepared as it is wanted, by agitating the salt with cold water, since, if kept for a length of time, or if heated, this solution easily undergoes decomposition; it is chiefly used in the separation of cobalt and nickel.

For carbonate of soda, we refer to the article on blowpipe-reagents (p. 106).

Biborate of soda has also been mentioned as a blowpipe-reagent (p. 107), and as this is its only use, we have nothing further to add in this place.

Hydrate of lime, used as a reagent, should be introduced into well-closed bottles when freshly slaked; it should be free from lumps of silicate, and must not effervesce very strongly with hydrochloric acid; hydrate of lime is used to liberate ammonia from its compounds, in order to the detection of this substance.

SPECIAL REAGENTS EMPLOYED IN SOLUTION.

Sulphurous Acid.—The solution of sulphurous acid employed in analysis is prepared by passing the gas through water till the latter is saturated; it is used as a reducing agent, and chiefly to convert arsenic into arsenious acid, in the course of detecting the bases.

Oxalic acid is occasionally contaminated with nitric acid, which may be detected by its property of bleaching solution of indigo upon the application of heat. Oxalic acid is used as a test for lime. One part of the crystals of oxalic acid may be dissolved in ten parts of water.

Hydrofluosilicic Acid.—This acid is employed as a test for baryta, and is liable to be contaminated with oxide of lead, which may be detected by hydrosulphuric acid. The introduction of this impurity may be avoided by keeping the acid in bottles of German glass. Hydrofluosilicic acid should produce no precipitate in solutions of the chlorides of strontium and calcium.

Sulphate of Potassa.—Solution of sulphate of potassa is prepared by dissolving, in hot water, a larger quantity of the salt than will be retained in solution at the ordinary temperature; the cold saturated solution is preserved for use. This reagent is used in the separation of strontia from lime.

The *bichromate of potassa* of commerce may be used in analysis; one part of the crystals may be dissolved in twelve parts of water.

Acetate of potassa is used where it is desired to replace a strong acid (e. g. hydrochloric or nitric acid) by acetic acid; it should not effervesce with acids, and its solution must not be tinged by sulphide of ammonium. It may be dissolved in three parts of water.

Ferricyanide of Potassium.—To prepare the solution of this salt, the crystals may be shaken with water till no more is dissolved; the solution should give no precipitate, but merely a dark color, with sesquichloride of iron.

Sulphite of Ammonia.—A solution of sulphite of ammonia, prepared by saturating a solution of ammonia with sulphurous acid, is sometimes substituted for this latter in reducing arsenic acid.

Baryta-water is prepared by heating the crystals of baryta with water, till no more is dissolved; the solution should be kept in well-stoppered bottles nearly filled, or it is liable to absorb carbonic acid from the air, and to deposit carbonate of baryta.

The *sulphate of magnesia* of commerce is generally sufficiently pure for analytical purposes; a cold saturated solution will be found most convenient.

Nitrate of cobalt has been already alluded to as a blowpipe-reagent (p. 107).

Sulphate of Manganese.—A moderately dilute solution of this salt is employed as a test for hypochlorites.

Acetate of Lead.—Solution of acetate of lead is prepared by dissolving one part of the crystallized salt in 6 parts of water; it is chiefly used as a test for chromic and hydrosulphuric acids.

Sulphate of Copper.—In order to prepare a solution of sulphate of copper, one part of the crystals is dissolved in ten parts of water; the use of this reagent is very limited.

Chloride of Mercury.—One part of chloride of mercury is dissolved in twenty parts of water. It is used chiefly as a test for tin.

Chloride of Tin.—A solution of this salt is useful as a test for gold; it is best prepared by boiling granulated tin with dilute hydrochloric acid as long as it is rapidly dissolved; the supernatant liquid may then be decanted, and mixed with about half its volume of the dilute acid; if this last precaution be neglected, the solution soon becomes opaque.

Bichloride of platinum in the form of a strong solution (containing about 5 per cent. of the metal) is used as a test for potassa; it should not contain a great excess of free acid, and when evaporated to a thick syrup, should form a perfectly clear solution in alcohol.

Nitrate of Silver.—Solution of nitrate of silver is prepared by dissolving one part of the crystals in eight parts of water, and is particularly useful in testing for acids. This solution should be perfectly neutral to blue litmus, and must be free from copper, which would be indicated by a blue color upon addition of excess of ammonia.

Alcohol—The *spiritus vini rectificatissimus* of the druggist is sufficiently strong for the limited application which it receives in qualitative analysis. It should not become turbid upon addition of water, nor leave any residue when evaporated.

Ether.—Rectified ether should be employed when required in analysis. It is almost exclusively used in testing for bromine.

Solution of indigo in fuming sulphuric acid (termed *sulphindigotic acid*) is employed for the detection of nitric acid and free chlorine or its oxides.

SPECIAL REAGENTS PRESERVED IN THE SOLID STATE.

Chlorate of potassa is a very useful oxidizing agent, and is employed, in conjunction with hydrochloric acid, to dissolve sulphur, and to remove organic matters which would interfere in analysis.

Phosphate of soda and ammonia will be found among the blowpipe reagents (p. 107).

Hydrate of Baryta.—Dry (not crystallized) hydrate of baryta is used in the decomposition of insoluble silicates in order to test them for alkalies; it should therefore be free from these latter, which may be ascertained by dissolving in dilute hydrochloric acid, precipitating the baryta by ammonia and sesquicarbonate of ammonia, with the aid of heat, filtering and evaporating to dryness, when no residue should be left.

Dry chloride of calcium, obtained by drying the crystals upon a sand-bath, is employed in desiccating gases. It should not possess an alkaline reaction.

Carrara marble is necessary for evolving carbonic acid in testing for arsenic by the method of Fresenius.

Sulphate of Iron.—Pure green crystals of sulphate of iron are employed for analytical purposes; it is used chiefly in testing for nitric and hydrocyanic acids. This salt is always preserved in the solid state, since the solution rapidly absorbs oxygen from the air; when required in solution, the crystals should be shaken with cold water.

Binocide of Manganese.—This substance is useful for evolving chlorine; it need not be chemically pure, but should be free from any considerable quantity of carbonate of lime, which may be detected by the effervescence with dilute nitric acid.

Granulated zinc is employed in analysis chiefly for the disengagement of hydrogen; it will therefore, in general, be sufficiently pure if the gas which is disengaged by it from dilute sulphuric acid be free from antimony and arsenic, which may be ascertained by Marsh's test, to be described hereafter. If the zinc should be required for other purposes, it must be remembered that it is liable to contain lead and tin, the former of which is left behind in the form of black scales on boiling the zinc with dilute hydrochloric acid, and the latter may be detected by

mixing the hydrochloric solution with chloride of mercury, which will yield a precipitate of the subchloride of mercury.

Copper.—This metal is especially useful for the reduction of mercury and arsenic from their solutions; it should be employed either in the form of thin sheet copper, cut into strips of about one inch by $\frac{1}{4}$ inch, or in rather thin wire, cut into lengths of an inch. It should be cleaned before use, by allowing it to remain for a few seconds in concentrated nitric acid, and then washing with water.

Starch.—Ordinary white starch is used in the detection of bromine and iodine.

Sulphur.—Flowers of sulphur are employed occasionally; this substance should leave no residue when heated in a porcelain crucible.

Sulphide of iron is largely used for the evolution of sulphuretted hydrogen; it should be pretty compact and homogeneous, no iron filings being visible. It is employed in fragments of the size of a bean.

DISTILLED WATER.—Above all things, it is of course necessary that the distilled water employed in analysis be carefully examined. It must leave no trace of residue when an ounce or so is evaporated in a clean platinum dish; it must not produce the slightest turbidity with nitrate of silver, chloride of barium, or oxalate of ammonia.

ANALYTICAL CLASSIFICATION OF THE METALS.

§ 334. In order to acquire, with the least expenditure of time, a practical knowledge of qualitative analysis, this study may be divided into two parts; in the first part, our object is to acquaint ourselves with the reactions of the inorganic bases and acids, and afterwards, with those of the organic acids; and the knowledge thus obtained will be applied in the second part to the general course of qualitative analysis, *i. e.* to effect the detection of these bases and acids, and their separation from each other.

It would as far exceed the limits, as it would be foreign to the design of a work of this nature, to give a complete description of the reactions of all known acids and bases, and we shall therefore confine ourselves to those which are generally met with in the arts and manufactures, and in pharmacy, the number of which is comparatively small; the reactions of the rarer metals have been described in former pages.

For the sake of convenience, and as an aid to the memory, the metallic oxides are divided into *five* groups.

In the *first* group are included the three alkalies, *potassa*, KO, *soda*, NaO, and *oxide of ammonium (ammonia)*, NH₄O, which are not precipitated by any of the reagents employed in separating the other groups, and are detected by special tests.

The *second* group consists of *baryta*, BaO, *strontia*, SrO, *lime*, CaO, and *magnesia*, MgO, which are not precipitated by hydrochloric acid, by hydrosulphuric acid, by ammonia in the presence of chloride of ammonium, nor by sulphide of ammonium; the three former, baryta, strontia, and lime, are thrown down as carbonates when sesquicarbonate of ammonia is added to their solutions, in presence of chloride of ammonium and free ammonia, whilst magnesia is not precipitated by this reagent, but separates as a phosphate upon addition of phosphate of soda.

The oxides contained in the *third* group are such as are not precipitated from their solutions by hydrochloric acid, or by hydrosulphuric acid in the presence of free hydrochloric acid, but which are separated, either as hydrated oxides or as sulphides, on the addition of ammonia in excess, and of sulphide of ammonium, even if chloride of ammonium be present in the solution.

This group comprehends *alumina*, Al₂O₃, the *oxides of iron* FeO and Fe₂O₃,

sesquioxide of chromium, Cr_2O_3 , *oxide of cobalt*, CoO , *oxide of nickel*, NiO , *oxide of manganese*, MnO , and *oxide of zinc*, ZnO .

In the *fourth* group, we find those oxides the solutions of which are not precipitated by hydrochloric acid, but yield, on addition of hydrosulphuric acid, the sulphides corresponding to the oxides; the metals of this group, therefore, form sulphides insoluble in water and in dilute hydrochloric oxide.

The oxides which compose this group are *oxide of mercury*, HgO , *oxide of lead*, PbO , *teroxide of bismuth*, BiO_3 , *oxide of copper*, CuO , *oxide of cadmium*, CdO , *teroxide of gold*, AuO_3 , *binocide of platinum*, PtO_2 , *teroxide of antimony*, SbO_3 , *antimonic acid*, SbO_3 , *oxide of tin*, SnO , *binocide of tin*, SnO_2 , *arsenious acid*, AsO_2 , *arsenic acid*, AsO_3 .

The *fifth* group includes those metallic oxides, the chlorides corresponding to which are insoluble, or soluble with difficulty, in water; the solutions of these oxides, therefore, are precipitated by hydrochloric acid. The members of this group are *oxide of silver*, AgO , *suboxide of mercury*, Hg_2O , and *oxide of lead*, PbO .¹

In the table on next page all the metals are arranged on the principles here developed.

¹ Oxide of lead is found in the preceding group as well as in this, since the chloride of lead is not quite insoluble in water, and therefore some lead will escape precipitation by hydrochloric acid, but may be thrown down as sulphide by hydrosulphuric acid.

ANALYTICAL CLASSIFICATION OF THE METALS.

** When no color is stated, the precipitate is white. Slight differences in tint are not noticed, since it would be unsafe to draw any conclusions from them.

GROUP I.	GROUP II.	GROUP III.	GROUP IV.	GROUP V.
Potassium Sodium <i>Lithium</i> Ammonium	CHLORIDE OF AMMONIUM, AMMONIA, and CARBON- ATE OF AMMONIA.	CHLORIDE OF AMMONIUM, AMMONIA, and SUL- PHIDE OF AMMONIUM.	HYDROSULPHURIC ACID <i>In acid solutions.</i>	HYDROCHLORIC ACID.
	<p><i>Precipitated,</i> Barium Strontium Calcium, <i>as</i> Carbonates</p> <p><i>Not precipitated,</i> Magnesium, <i>the carbonate being soluble in chloride of ammonium.</i></p>	<p><i>Precipitated</i> <i>as oxides,</i> Aluminum Chromium, <i>green</i> <i>Glucinum</i> <i>Thorinum</i> Zirconium Cerium <i>Lanthonium</i> <i>Didymium</i> Yttrium Erbium Terbium Titanium Tantalum Niobium <i>Pelopium</i></p> <p><i>as sulphides,</i> <i>as FeS black</i> Iron Nickel Cobalt Manganese Zinc Uranium Vanadium</p> <p><i>as FeS black</i> " NiS " " CoS " " MnS buff " ZnS white " U₃S₈ black " VS₃ "</p>	<p><i>as CuS black</i> " BiS₃ " " PbS " " HgS " " AuS₃ " " PtS₃ " " Rh₂S₃ " " IrS₃ " " Ru₂S₃ " " OsS₃ brown-yellow " TeS₃ black " WS₃ brown " MoS₃ " " CdS yellow " AsS₃ " " AsS₅ " " SnS₂ " " SnS black " SbS₃ orange " SbS₅ "</p> <p>Copper Bismuth Lead Mercury Gold Platinum <i>Palladium</i> <i>Rhodium</i> <i>Iridium</i> <i>Ruthenium</i> <i>Osmium</i> <i>Tellurium</i> <i>Tungsten</i> <i>Molybdenum</i> Cadmium Arsenic " " Tin " " Antimony " "</p>	<p>Lead Silver Mercury</p> <p><i>as PbCl.</i> " AgCl. " HgCl.</p>

REACTIONS OF THE METALLIC OXIDES.

It will be observed, in the following account of the behavior of metallic oxides with reagents:—

1. That, unless mention to the contrary is made, a solution of a *neutral* salt of the oxide under examination is supposed to be operated upon.

2. That, at the commencement of each section, we shall name the most convenient form in which the oxide may be examined.

3. That the term *compound of an oxide* is applied not only to those substances which actually contain the oxide in question, but also to such haloid compounds (chlorides, *e.g.*) as correspond to that oxide; thus, the chloride of mercury is spoken of as a compound of the oxide of mercury, since it resembles such a compound in most of its reactions.

4. That, in general, only those reactions are set down which admit of practical application in the systematic course of analysis, those which possess merely a general interest being omitted.

The student is cautioned against supposing that any reaction which is ascribed to one oxide (and not to others of the same group) may serve as a characteristic test for that oxide, since such an application will always receive especial notice, and the reaction is omitted in the case of the other oxides, merely because it is not applied in the systematic course of analysis.

§ 335. FIRST GROUP.

Oxides which are not precipitated by the reagents employed to separate the other groups.

POTASSA, KO. SODA, NaO. OXIDE OF AMMONIUM, NH₄O.

POTASSA, KO.

Solution best fitted for the reactions: Chloride of Potassium, KCl.¹

BICHLORIDE OF PLATINUM; an orange-yellow, heavy, crystallizing precipitate of the *double Chloride of Platinum and Potassium* (KCl.PtCl₂); somewhat soluble in *water*, insoluble in *alcohol*; not more soluble in *dilute acids* than in *water*. In dilute solutions, this precipitate is formed only after some time; the precipitation is promoted by agitation. The most delicate method of applying this test is to mix the solution with bichloride of platinum, to evaporate to dryness upon a water-bath, and to digest the residue with *alcohol*, when crystals of the double-salt will be left undissolved; the addition of bichloride of platinum should always be preceded by that of *hydrochloric acid*, to convert the potassium into chloride, if it should not exist already in that form.

TARTARIC ACID, in rather concentrated solutions, especially on agitating violently, a white crystalline precipitate of *Acid Tartrate (Bitartrate) of Potassa* (KO.HO.T); soluble to a considerable extent in *water*; very readily soluble in *mineral acids*, and in *alkalies*. This precipitate is generally deposited only after some time.

BLOWPIPE.—Compounds of potassium, heated on a thin platinum wire, in the *reducing flame*, impart a *violet colour* to the *outer flame*. This reaction is not visible when the compound contains even a moderate quantity of soda, though, in some cases, the violet flame of the potassium is seen for an instant after the

¹ In the first group, the chlorides may always be used to exhibit the reactions.

yellow colour of the (more easily reducible) sodium has disappeared. Before applying this test, the operator must assure himself that the wire itself does not impart a yellow color to the outer flame. (The wire must be repeatedly washed with distilled water, and heated in the inner flame until it no longer imparts any color.)

SODA, NaO.

If a solution of soda be mixed with excess of HYDROCHLORIC ACID and BI-CHLORIDE OF PLATINUM, and gently evaporated in a watch-glass, on a water-bath, radiated needles of the *double Chloride of Platinum and Sodium* (NaCl.PtCl_2) will be deposited.

BLOWPIPE.—Compounds containing sodium, when exposed, on a thin (well-cleansed) platinum wire, to the *reducing-flame*, communicate a *golden-yellow color* to the *oxidizing flame*. This test is exceedingly delicate, permitting the detection of the least trace of soda.

There exists no test which can be depended upon for the precipitation of small quantities of soda in solution.

OXIDE OF AMMONIUM, NH_4O .

A red heat always volatilizes oxide of ammonium, in whatever form of combination it may exist; if it be combined with a fixed acid (as phosphoric, boracic, &c.), the latter is left in the residue.

HYDRATE OF LIME, with the aid of a gentle heat, evolves *ammonia* (NH_3), which may be recognized: 1, by its *pungent odour*, 2, by its *alkaline reaction* to moistened test-papers, and 3, by the *white clouds* which it produces on the approach of a glass rod, moistened with moderately *dilute hydrochloric* or *nitric acid* (diluted to the point at which they cease to fume in the air). The ammoniacal compound (either solid or dissolved) should be stirred in a small dish, with dry hydrate of lime and a little water, and gently heated on a sand-bath.

TARTARIC ACID, in rather concentrated solutions, a white crystalline precipitate of *Acid Tartrate (Bitartrate) of Oxide of Ammonium* ($\text{NH}_4\text{O.HO.T}$), similar in its characters to the bitartrate of potassa.

BICHLORIDE OF PLATINUM; a light-yellow crystalline precipitate of the *double Chloride of Platinum and Ammonium* ($\text{NH}_4\text{Cl.PtCl}_2$), very similar in its reactions to the corresponding potassium-compound.

§ 336. SECOND GROUP.

Oxides which are precipitated from their solutions as carbonates by the carbonates of the alkalis.

—BARYTA, BaO . STRONTIA, SrO . LIME, CaO . MAGNESIA, MgO .
BARYTA, BaO .

Solution best fitted for the reactions: Chloride of Barium, BaCl .

SESQUICARBONATE OF AMMONIA; white precipitate of *Carbonate of Baryta* (BaO.CO_2), readily soluble in *hydrochloric acid*. In order that the precipitation may be complete, some free *ammonia* should be added, and a moderate heat applied to the solution, to decompose any (*soluble*) bicarbonate of baryta which might be formed.

OXALATE OF AMMONIA; white precipitate of *Oxalate of Baryta* (BaO.O), soluble in *hydrochloric acid*.

SULPHURIC ACID (*dilute*); white precipitate of *Sulphate of Baryta* (BaO.SO_2) (even in very dilute solutions) insoluble in *dilute acids*.

SULPHATE OF POTASSA gives the same precipitate.

SULPHATE OF LIME also gives immediately a precipitate of *Sulphate of Baryta*.

HYDROFLUOSILICIC ACID; a white precipitate of *Silicofluoride of Barium* ($8\text{BaF} \cdot 2\text{SiF}_6$), insoluble in *dilute acids*; this precipitate is very transparent, and is formed only after some time in dilute solutions; in order to separate baryta completely from a solution by this reagent, it is better to evaporate to dryness, and to treat the residue with strong *alcohol*, which leaves all the silicofluoride of barium undissolved.

PHOSPHATE OF SODA; white precipitate of *Phosphate of Baryta* ($2\text{BaO} \cdot \text{H}_3\text{PO}_4$), soluble in *hydrochloric acid*.

BLOWPIPE.—Compounds of barium, strongly heated, on a thin platinum wire, in the *inner flame*, impart a *light green* color to the *outer flames*; insoluble compounds should be moistened with a little *dilute hydrochloric acid* before applying this test.

STRONTIA, SrO.

Solution best fitted for the reactions: Chloride of Strontium, SrCl.

SESQUICARBONATE OF AMMONIA; the same reaction as in the case of baryta.

OXALATE OF AMMONIA; same as with baryta.

SULPHURIC ACID (*dilute*); white precipitate of *Sulphate of Strontia* ($\text{SrO} \cdot \text{SO}_3$), which, being somewhat soluble in water, is not formed immediately in a dilute solution; insoluble, or nearly so, in *dilute acids*.

SULPHATE OF POTASSA produces the same precipitate; if a solution of strontia be mixed with an excess of sulphate of potassa, evaporated to dryness, and the residue boiled with *water*, the latter will dissolve so little sulphate of strontia, that *oxalic acid* will not produce a precipitate in the solution.

SULPHATE OF LIME, even in concentrated solutions of strontia, gives a precipitate only after standing for some time (varying with the strength of the solution of strontia).

PHOSPHATE OF SODA; same as with baryta.

BLOWPIPE.—Compounds of strontium, strongly heated, on a thin platinum wire, in the *reducing flame*, color the *oxidizing flame* most intensely *carmine-red*; insoluble compounds should first be moistened with *dilute hydrochloric acid*.

LIME, CaO.

Solution best fitted for the reactions: Chloride of Calcium, CaCl.

SESQUICARBONATE OF AMMONIA; a white precipitate of *Carbonate of Lime* ($\text{CaO} \cdot \text{CO}_2$), which becomes far less voluminous on heating the solution; some free ammonia should be added in this reaction, and only a moderate heat applied; for if the solution is boiled, the ammoniacal salt may decompose the carbonate of lime, reproducing a soluble compound of that base, in consequence of the great volatility of the carbonate of ammonia. The precipitate dissolves very readily in *hydrochloric acid*.

OXALATE OF AMMONIA; white precipitate of *Oxalate of Lime* ($\text{CaO} \cdot \bar{\text{O}}$), soluble in *hydrochloric acid*; this precipitate being produced even in very dilute solutions, especially if a little free ammonia be added, oxalate of ammonia becomes a very delicate test for lime, but will not serve to distinguish it from baryta and strontia.

SULPHURIC ACID (*dilute*), only in concentrated solutions, a white precipitate of *Sulphate of Lime* ($\text{CaO} \cdot \text{SO}_3$), soluble in much water.

SULPHATE OF POTASSA, only in concentrated solutions; if a solution containing lime be mixed with an excess of sulphate of potassa, evaporated to dryness, and the residue boiled with *water*, so much sulphate of lime is dissolved that the solution gives a precipitate with *oxalic acid*.

PHOSPHATE OF SODA; white gelatinous precipitate of *Phosphate of Lime* (2CaO.HO.PO_3), soluble in *dilute acids*.

BLOWPIPE.—Compounds of lime, heated on a thin platinum wire, in the *inner flame*, impart an *orange-red* color to the *outer flame*; insoluble compounds of lime should be moistened with *dilute hydrochloric acid*.

MAGNESIA, MgO .

Solution best fitted for the reactions: Sulphate of Magnesia, MgO.SO_4 .

SESQUICARBONATE OF AMMONIA; no precipitate in the cold, but, on boiling, a white precipitate of *Basic Carbonate of Magnesia* which contains only part of the magnesia, the remainder existing in solution as a double-salt of magnesia and oxide of ammonium. The precipitate dissolves readily in *chloride of ammonium*, so that the addition of this salt to the magnesia-solution would prevent the production of a precipitate.

AMMONIA; white precipitate of *Hydrate of Magnesia* (MgO.HO) which contains only half of the magnesia present; for



Hydrate of magnesia is soluble in *chloride of ammonium*, so that ammonia produces no precipitate in a solution of magnesia containing chloride of ammonium.

POTASSA; white precipitate of *Hydrate of Magnesia*, insoluble in excess.

BARYTA precipitates the whole of the magnesia in the same form, provided the solution be free from ammoniacal salts.

CHLORIDE OF AMMONIUM, AMMONIA, AND PHOSPHATE OF SODA, produce, even in very dilute solutions, a white, highly crystalline precipitate of *Phosphate of Magnesia and Oxide of Ammonium* ($2\text{MgO.NH}_4\text{O.PO}_3$); slightly soluble in water, less so in solution of ammonia, and readily soluble in *dilute acids*. In dilute solutions, the precipitate is only deposited after some time; its formation is much promoted by violent agitation.

BLOWPIPE.—Solid compounds of magnesia, strongly heated on *charcoal*, leave a *white, infusible, highly incandescent mass*; if this be moistened with *nitrate of cobalt*, and again strongly heated, a *pale rose-colored compound* is produced, the color of which is more visible on cooling.

THIRD GROUP.

§ 337. *Oxides, the solutions of which are not precipitated by Hydrochloric or Hydrosulphuric Acid, but which are precipitated, either as hydrates or as sulphides, by Sulphide of Ammonium in the presence of Chloride of Ammonium and Ammonia.*

ALUMINA (Al_2O_3)	OXIDE OF COBALT (CoO)
SESQUIOXIDE OF CHROMIUM (Cr_2O_3)	OXIDE OF NICKEL (NiO)
SESQUIOXIDE OF IRON (Fe_2O_3)	OXIDE OF MANGANESE (MnO)
OXIDE OF IRON (FeO)	OXIDE OF ZINC (ZnO)

ALUMINA, Al_2O_3 .

Solution best fitted for the reactions: Alum, $\text{Al}_2\text{O}_3.3\text{SO}_3.\text{KO.SO}_4$.

AMMONIA, even in presence of chloride of ammonium; a very gelatinous, semi-transparent precipitate of *Hydrate of Alumina*; more visible when the liquid is heated; slightly soluble in excess of ammonia, and reprecipitated on boiling (this solution in excess does not take place if a sufficient quantity of

chloride of ammonium be present); soluble in *hydrochloric acid* (though with some difficulty, unless freshly precipitated). The presence of fixed organic matters (*sugar, tartaric acid, &c.*) interferes with the precipitation.

SULPHIDE OF AMMONIUM; the same precipitate of *Hydrate of Alumina*, hydrosulphuric acid being evolved.

POTASSA; a similar precipitate of *Hydrate of Alumina*; readily soluble in an excess; completely reprecipitated by adding an *excess of acid*, and subsequently *excess of ammonia*. SILICATE OF POTASSA also precipitates the whole of the alumina from this solution, in the form of *Silicate of Alumina*, which is insoluble in potassa.

PHOSPHATE OF SODA, a white precipitate of *Phosphate of Alumina*; soluble in *strong mineral acids*, and reprecipitated by *ammonia*; insoluble (or nearly so) in *acetic acid*; readily soluble in *potassa*, and reprecipitated by an *excess of acetic acid*; if *silicate of potassa* be added to the alkaline solution of phosphate of alumina, the alumina is precipitated, the phosphoric acid remaining in solution.

BLOWPIPE.—Solid compounds of alumina strongly heated on *charcoal* leave a *white, infusible, and highly incandescent residue*; if this be moistened with solution of *nitrate of cobalt*, and again strongly heated, it furnishes a *blue mass*; this behavior, however, is not characteristic of alumina, since some other substances (especially phosphates) exhibit the same reaction.

SESQUIOXIDE OF CHROMIUM, Cr_2O_3 .

Solution best fitted for the reactions: Sesquichloride of Chromium, Cr_2Cl_7 .

AMMONIA, even in presence of *chloride of ammonium*; a greenish-blue precipitate of *Hydrated Sesquioxide of Chromium*; slightly soluble in an excess, forming a pink solution, from which the sesquioxide is reprecipitated by boiling; readily soluble in *acids*. The presence of *fixed organic matters* interferes with the precipitation.

SULPHIDE OF AMMONIUM; the same precipitate of *Hydrate*, sulphuretted hydrogen being evolved.

POTASSA; a precipitate of *Hydrated Sesquioxide*, readily soluble in excess; reprecipitated entirely by boiling, provided no fixed organic matters be present; if a very large excess of potassa be employed, prolonged ebullition is necessary to reprecipitate the sesquioxide. When mixed with a considerable quantity of sesquioxide of iron, the sesquioxide of chromium is not dissolved by an excess of potassa.

Solid compounds containing chromium, when fused (on platinum-foil) with *nitrate of potassa* and a little *carbonate of soda* (the blowpipe-flame being directed upon the under surface of the foil), yield a yellow mass of *Alkaline Chromate* (NaO CrO_3) which may be dissolved in *water*, and tested for *Chromic Acid*, by adding excess of *acetic acid* and *acetate of lead*, which gives a yellow precipitate of *lead chromate*. This test is applicable under all circumstances, and permits the detection of very small quantities of chromium.

BLOWPIPE.—Sesquioxide of chromium, fused with a bead of *borax*, in the *oxidizing flame*, yields a *yellow glass*, which assumes a *bright emerald-green color* in the *reducing flame*.

SESQUIOXIDE OF IRON, Fe_2O_3 .

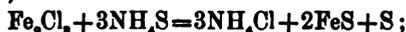
Solution best fitted for the reactions: Sesquichloride of Iron, Fe_2Cl_6 .

AMMONIA, even in the presence of *chloride of ammonium*: a reddish-brown, flocculent precipitate of *Hydrated Sesquioxide of Iron*, insoluble in excess; readily soluble in *acids*. The presence of *fixed organic matters* (*tartaric acid, &c.*) prevents the precipitation.

SULPHIDE OF AMMONIUM; a reddish-brown precipitate of *Hydrated Sesquioxide of Iron*, insoluble in excess; readily soluble in *acids*.

mineral acids (as well as in sesquichloride of iron), a white precipitate of *Sulphur*, the hydrogen of the hydrosulphuric acid serving to reduce the *sesqui*-compound of iron to a *proto*-compound. In a solution of a compound of sesquioxide of iron with a weak acid, as in acetate of sesquioxide of iron (or sesquichloride of iron mixed with excess of acetate of potassa), *hydrosulphuric acid* not only reduces the *sesquioxide* to *oxide*, with separation of *Sulphur*, but precipitates the whole of the iron as *black sulphide* (FeS) provided there be not too great an excess of free organic acid present.

SULPHIDE OF AMMONIUM; a black precipitate of *Sulphide of Iron* (FeS), mixed with *Sulphur*,



soluble with difficulty in *acetic acid*; readily dissolved by *mineral acids*. When the quantity of this precipitate is very small, it has a greenish tinge. In solutions containing much fixed organic matter (*tartaric acid*, &c.), the precipitate appears to be partly dissolved by an excess of sulphide of ammonium, imparting a dark green color to the liquid, but the precipitation is complete on boiling.

POTASSA; the red-brown precipitate of *Hydrate*; insoluble in excess;¹ readily soluble in *acids*. Fixed organic matters prevent the precipitation.

ACETATE OF POTASSA; a fine red liquid, due to the formation of *Acetate of Sesquioxide of Iron* ($\text{Fe}_2\text{O}_3 \cdot 3\bar{\text{A}}$).

FERROCYANIDE OF POTASSIUM; a dark blue precipitate (*Prussian Blue*, Fe_4Cfy_6) of *Sesquiferrocyanide of Iron*; insoluble in *acids* (except *oxalic*); decomposed by *alkalies*. This is an exceedingly delicate test for sesquioxide of iron; in very dilute solutions, merely a blue tinge is produced, and after long standing, a blue precipitate is formed at the bottom of the vessel. It is always advisable to acidify solutions with *acetic acid* before applying this test; should a free mineral acid be present, the addition of ferrocyanide of potassium should be preceded by that of an excess of *acetate of potassa*, in order to substitute free acetic acid for the mineral acid, which would decompose the ferrocyanide of potassium, giving rise to a blue color.

FERRICYANIDE OF POTASSIUM produces merely a *dark brown color*.

SULPHOCYANIDE OF POTASSIUM gives a deep *blood-red color* (due to *Sesquisulphocyanide of Iron*, Fe_2Csy_2) which disappears on the addition of *alkalies* or of a large excess of a *strong acid*. This test detects very small quantities of sesquioxide of iron, and may be applied to moderately acid solutions.

BLOWPIPE.—Compounds containing iron, when fused with a bead of *borax*, upon platinum wire, yield, in the *oxidizing flame*, a *brownish-red glass*, which assumes a dirty (*bottle*-) *green color* in the *inner flame*, from the reduction of the sesquioxide of iron to the magnetic (*proto-sesqui*) oxide (Fe_3O_4).

OXIDE OF IRON, FeO .

Solution best fitted for reactions: Sulphate of Oxide of Iron, $\text{FeO} \cdot \text{SO}_4$.²

HYDROSULPHURIC ACID gives no precipitate even in neutral solutions of the salts of oxide of iron with the strong (mineral) acids, but in those with weak (organic) acids, it produces a black precipitate of Sulphide of Iron (FeS); the whole of the iron may be precipitated in this way, if there be not too great an excess of the organic acid. The characters of this precipitate have been already given (*see above*). From *alkaline* solutions, *hydrosulphuric acid* also throws down the whole of the iron.

¹ If much sesquioxide of chromium be present, considerable quantities of sesquioxide of iron may be dissolved by the potassa.

² The solution should be freshly prepared for each experiment, as it absorbs oxygen so rapidly when exposed to the air.

SULPHIDE OF AMMONIUM; a black precipitate of *Sulphide of Iron* (FeS). The remarks made at p. 515 hold good also in this case.

AMMONIA; a light-colored precipitate of *Hydrated Oxide of Iron* (FeO.HO) which rapidly absorbs oxygen from the air, passing, first, into the dirty-green *Magnetic Oxide*, and ultimately into red-brown *Sesquioxide of Iron*; the precipitate at first produced contains only half the iron present, the remainder existing in solution as a *double-salt of Oxide of Iron and Oxide of Ammonium*:—



but when the supernatant liquid (containing excess of ammonia) is exposed to air, it absorbs oxygen, and deposits the whole of the iron in the form of *Sesquioxide*.

If *chloride of ammonium* (or other ammoniacal salt) be added to the solution of oxide of iron, ammonia will not produce any precipitate in it, but the solution, when exposed to the air, absorbs oxygen, and deposits the sesquioxide.

POTASSA; the same precipitate of *Hydrated Protoxide*, which rapidly absorbs oxygen.

NITRIC ACID, added to a cold solution of oxide of iron, produces a transient brown color, due to a compound of the iron-salt with *dioxide of nitrogen* (see p. 341); the brown color disappears on heating, giving place to a yellow, the whole of the iron being converted into sesquioxide.

FERROCYANIDE OF POTASSIUM; a light blue (said to be white when absolutely pure) precipitate of a *Double Ferrocyanide of Potassium and Iron* [$\text{KFe}_3\text{Cfy}_3 = \frac{1}{2}(\text{K}_2\text{Cfy}_2, 3\text{Fe}_2\text{Cfy}_2)$]:—



this precipitate is insoluble in *dilute acids*, and eagerly absorbs oxygen from the air, being converted into a mixture of *Prussian blue* and oxide of iron (which is dissolved by the free acid if any be present):—



this reaction is visible even in very dilute solutions; free *alkalies* prevent the formation of a precipitate.

FERRICIANIDE OF POTASSIUM; a dark blue precipitate of *Ferricyanide of Iron* (Fe_3Cfy_2); insoluble in *dilute acids*; decomposed by *alkalies*; the same remarks hold good with regard to the delicacy of this test and to the precautions necessary in its application, as were made respecting the ferrocyanide of potassium as a test for sesquioxide of iron (see p. 515). This test serves to distinguish the two oxides of iron.

BLOWPIPE—Compounds of oxide of iron may be tested before the blowpipe in the same way as those of the sesquioxide.

OXIDE OF COBALT, CoO .

Solution best fitted for the reactions: Nitrate of Cobalt, CoO.NO_3 .

SULPHIDE OF AMMONIUM: a black precipitate of *Sulphide of Cobalt* (CoS); very sparingly soluble in *hydrochloric acid*, soluble in *nitric acid*.

AMMONIA: a bluish precipitate of a *Basic Salt of Cobalt* (this precipitate contains only part of the oxide, the rest remaining in solution as a double-salt, with the salt of oxide of ammonium produced in the reaction); readily soluble in excess of ammonia, forming a *reddish-brown solution* which becomes deeper in color (from absorption of oxygen) when exposed to air.

If the solution contain a sufficient quantity of an ammoniacal salt (or a free acid), it is not precipitated by ammonia.

Or if the solution contain any free acid, which will produce an ammoniacal salt, upon addition of ammonia.

SESQUICARBONATE OF AMMONIA; a pink precipitate of *Carbonate of Cobalt* ($\text{CoO} \cdot \text{CO}_2$) readily soluble in excess, forming a *red solution*. The presence of *ammoniacal salts* prevents the precipitation.

POTASSA; a blue precipitate of a *Basic Salt of Cobalt* which, when boiled with the liquid, assumes a brownish-red color, being converted into the *Hydrated Oxide of Cobalt* ($\text{CoO} \cdot \text{HO}$), insoluble in excess of *potassa*, readily soluble in *acids*. If *ammoniacal salts* be present in the solution, potassa produces no precipitate, until the solution is boiled, when, the ammonia being expelled, the whole of the oxide of cobalt is precipitated.

CYANIDE OF POTASSIUM; a brownish precipitate of *Cyanide of Cobalt* (CoCy); readily soluble in excess, being converted (completely if the solution be boiled) into *Cobalticyanide of Potassium* ($\text{K}_2\text{Co}_2\text{Cy}_6 = \text{K}_2\text{CoCy}$); *dilute acids* produce no precipitate in this solution, since the *Hydrocobalticyanic Acid* (H_2CoCy) which is separated, is perfectly soluble in water. If the solution of cobalticyanide of potassium be strongly acidulated with *nitric acid* (which decomposes the excess of cyanide of potassium, producing a certain quantity of nitrate of potassa), evaporated to dryness, and the residue fused for some minutes over a lamp, the cobalticyanide is oxidized and decomposed; on washing the fused mass with hot water, the black *Oxide of Cobalt* is left, and may be tested before the blowpipe.

BLOWPIPE.—Compounds of cobalt, fused with a *borax-bead* in *either flame*, produce a beautiful *blue glass*; the cobalt must be employed in very small proportion.

OXIDE OF NICKEL, NiO.

Solutions best fitted for the reactions: Sulphate of Nickel, $\text{NiO} \cdot \text{SO}_3$.

SULPHIDE OF AMMONIUM; a black precipitate of *Sulphide of Nickel* (NiS); insoluble in *colorless sulphide of ammonium*, but soluble to some extent in the ordinary *yellow sulphide*, which contains an excess of sulphur, forming a dark dirty-brown solution, which deposits the whole of the sulphide of nickel when evaporated. Sulphide of nickel is very sparingly soluble in *hydrochloric acid*, but readily in *nitric acid*.

AMMONIA; a light green precipitate of *Hydrated Oxide of Nickel* ($\text{NiO} \cdot \text{HO}$), readily soluble in excess, forming a *purplish-blue solution*; this precipitate, however, as in the case of cobalt, contains only part of the nickel. In solutions of oxide of nickel, which contain much *ammoniacal salt* or *free acid*, ammonia produces no precipitate.

SESQUICARBONATE OF AMMONIA; a light green precipitate of *Carbonate of Nickel* ($\text{NiO} \cdot \text{CO}_2$) soluble in excess, to a *blue liquid*. The presence of *ammoniacal salt* (or *free acid*) prevents the precipitation.

POTASSA; an apple-green precipitate of *Hydrated Oxide of Nickel*; insoluble in excess; readily soluble in *acids*. The presence of *ammoniacal salts* interferes to some extent with this precipitation; and it is necessary to boil with *excess of potassa*, until all ammonia is expelled, in order to separate the oxide of nickel completely.

CYANIDE OF POTASSIUM; a yellowish-green precipitate of *Cyanide of Nickel* (NiCy); soluble in excess, forming a *double Cyanide of Nickel and Potassium* ($\text{NiCy} \cdot \text{KCy}$), from which *acids* reprecipitate the cyanide of nickel; this latter is decomposed by boiling with *potassa*, cyanide of potassium being formed, whilst *Oxide of Nickel* is left undissolved.

BLOWPIPE.—Compounds of nickel, fused with a *borax-bead*, in the *outer flame*, yield a *sherry-red glass*, which readily changes in the *inner flame* into a glass which has a *purplish-gray* color when it contains very little nickel, and a *dusky, turbid, gray, brown, or black* hue when the amount of nickel is more considerable; if a minute fragment of *nitre* be added to the bead after exposure to the

inner flame, and the glass again fused in the *outer flame*, it acquires a rich *purple* color. Owing to the difficulty which they find in producing a well-defined flame, inexperienced operators generally obtain a grayish bead with nickel-compounds, even in the *outer flame*.

OXIDE OF MANGANESE, MnO .

Solution best fitted for the reactions: Sulphate of Manganese, $MnO.SO_4$.

SULPHIDE OF AMMONIUM; a flesh-colored (buff) precipitate of *Sulphide of Manganese* (MnS); soluble in *hydrochloric* or *nitric acid*.

AMMONIA; a white precipitate of *Hydrated Oxide of Manganese*, which becomes brown almost immediately from absorption of oxygen from the air, and formation of a higher oxide; the precipitate only contains part of the manganese, the remainder being left in solution as an ammoniacal double-salt; the precipitate is insoluble in excess of ammonia.

No precipitate is produced by ammonia in solutions of manganese which contain much *free acid* or *ammoniacal salt*; but when the ammoniacal liquid is exposed to the air, it absorbs oxygen, and deposits brown flocks of *Hydrated Binoxide of Manganese*.

SESQUICARBONATE OF AMMONIA; a white precipitate of *Carbonate of Manganese* ($MnO.CO_2$), almost insoluble in excess (especially on *boiling*).

POTASSA; a white precipitate of *Hydrated Oxide of Manganese*, rapidly becoming brown when exposed to the air; insoluble in excess of potassa; readily soluble in *acids*.

The presence of *ammoniacal salts* in great measure prevents the precipitation.

Solid compounds of manganese, fused with *carbonate of soda* and a little *nitre* on platinum-foil, yield a *fine green mass* (*blue* on cooling) of *Manganate of Soda*; by this test, the very smallest quantities of manganese may be detected. When very small quantities of material are to be tested, the experiment is conveniently made upon a loop of platinum-wire, which is moistened and dipped in powdered *carbonate of soda*; the latter is fused into a bead, a little of the substance taken upon it, and then a minute fragment of *nitre*; on fusing the bead in the *outer blowpipe flame*, the green color will be produced; if it be exposed to the *inner flame*, however, the color vanishes.

BLOWPIPE.—Compounds of manganese, when fused with a *borax-bead* in the *outer flame*, impart a beautiful *violet-red* color to the glass, which gradually fades in the *inner flame*, ultimately disappearing altogether.

OXIDE OF ZINC, ZnO .

Solution best fitted for the reactions: Sulphate of Zinc, $ZnO.SO_4$.

SULPHIDE OF AMMONIUM; a white precipitate of *Sulphide of Zinc* (ZnS); soluble in *hydrochloric* or *nitric acid*.

AMMONIA; a white precipitate of *Hydrated Oxide of Zinc*, readily soluble in excess. The precipitate, in this case, does not contain the whole of the zinc. *Ammoniacal salts* prevent the precipitation.

SESQUICARBONATE OF AMMONIA; a white precipitate of *Basic Carbonate of Zinc*, soluble in excess. *Ammoniacal salts* prevent the precipitation.

POTASSA; a white precipitate of *Hydrated Oxide of Zinc*, readily dissolved by an excess; *hydrosulphuric acid*, added to the alkaline solution, produces a white precipitate of *Sulphide of Zinc*.

BLOWPIPE.—Solid compounds of zinc, exposed on charcoal to the *inner blowpipe flame*, yield a *highly incandescent mass*, which is *yellow* while hot, and becomes *white* on cooling; if this mass be moistened with solution of *nitrate of cobalt*, and again strongly heated, a *fine green* compound is produced.

Solid compounds of zinc, fused with carbonate of soda on charcoal, in the *reducing flame*, give an incrustation of *Oxide of Zinc*, which is *yellow* while hot, and becomes *white* upon cooling.

§ 338. FOURTH GROUP.

Oxides, the sulphides corresponding to which are insoluble in cold dilute mineral acids.

OXIDE OF LEAD (PbO).¹

OXIDE OF MERCURY (HgO)	TEROXIDE OF BISMUTH (Bi ₂ O ₃)
OXIDE OF COPPER (CuO)	OXIDE OF CADMIUM (CdO)
TEROXIDE OF GOLD (Au ₂ O ₃)	BINOXIDE OF PLATINUM (PtO ₂)
OXIDE OF TIN (SnO)	BINOXIDE OF TIN (SnO ₂)
TEROXIDE OF ANTIMONY (Sb ₂ O ₃)	ANTIMONIC ACID (SbO ₂)
ARSENIOUS ACID (As ₂ O ₃)	ARSENIC ACID (AsO ₂).

OXIDE OF MERCURY (HgO).

Solution best fitted for the reactions: Chloride of Mercury, HgCl.

HYDROSULPHURIC ACID, when added in small quantity, a white or yellow precipitate, which is a *Compound of Sulphide of Mercury with the undecomposed Salt* (see p. 465); an excess of the reagent converts this precipitate into black *Sulphide of Mercury* (HgS); insoluble in *dilute sulphuric, hydrochloric, or nitric acid* alone, but readily soluble in a *mixture of hydrochloric and nitric acids* with the aid of heat; soluble to a very slight extent in the *sulphides of potassium and ammonium*; dissolved in some measure by *hot concentrated hydrochloric acid*; converted into a white compound, but not dissolved to any extent, by boiling with *concentrated nitric acid*.

POTASSA; in small quantity, a brownish precipitate, which is a basic compound, and is converted into yellow *Hydrated Oxide of Mercury* when treated with an excess of *potassa*.

AMMONIA; a white precipitate (see p. 462) soluble to some extent in an excess, especially in the presence of *ammoniacal salts*.

METALLIC COPPER, introduced into a solution of mercury, especially after acidification with *hydrochloric acid*, becomes covered with a white, lustrous coating; when moderately heated, the copper regains its original color, vapors of mercury being evolved; this test is exceedingly delicate; slips of copper wire, about an inch in length, may be used; they should be cleaned by shaking for a few moments with concentrated nitric acid, and thoroughly washed; half a dozen such slips should be boiled for three or four minutes in the solution, previously acidulated with hydrochloric acid; they are then well rinsed, dried by pressure between blotting-paper, and heated in a glass tube of $\frac{1}{4}$ inch diameter, constructed so as to allow the passage of a feeble current of air; a coating of minute *Globules of Mercury* is formed upon the cool part of the tube; these may be united into larger globules by rubbing with a glass rod.

CHLORIDE OF TIN (SnCl) added in small quantity to a solution of oxide of mercury, produces a white precipitate of *Subchloride* (Hg₂Cl) which becomes gray, from reduction to the metallic state, on adding an excess of the reagent.

Solid compounds of mercury, mixed with a large excess (at least 12 parts) of

¹ The reactions of this oxide are given in the fifth group, to which it more properly belongs.

dry carbonate of soda, and heated in a perfectly dry tube of hard glass, having a diameter of about $\frac{1}{4}$ inch, and expanded into a bulb at one end, furnish minute globules of *Metallic Mercury* which are deposited on the cool part of the tube, and may be united into larger globules by rubbing with a glass rod. This test is exceedingly delicate; in order that it may be perfectly successful, the mercury-compound should be thoroughly dried (in a water-bath), and the carbonate of soda should be ignited immediately previous to use; in order to prevent the sublimation of undecomposed mercury-compounds, it is well to cover the mixture in the bulb-tube with a layer of pure carbonate of soda.

TEROXIDE OF BISMUTH, BiO_2 .

Solution best fitted for the reactions: Nitrate of Teroxide of Bismuth, $\text{BiO}_2 \cdot 3\text{NO}_3$.

HYDROSULPHURIC ACID; a black precipitate of *Tersulphide of Bismuth* (BiS_3); insoluble in cold *dilute acids* and in *alkaline sulphides*; soluble in *hot dilute nitric acid*.

WATER, added in large quantity to the salts of bismuth, decomposes them, with precipitation of a *white basic salt*; the terchloride exhibits this behavior in the most striking manner, provided too large an excess of free acid be not present; in order to apply this test to any compound of bismuth (except the sulphate), an excess of *hydrochloric acid* is added, the solution evaporated just to dryness, the residue allowed to cool, redissolved in a little water with addition of a single drop of hydrochloric acid, and the clear liquid largely diluted with water, when a milkiness is produced, caused by the minute particles of a highly crystalline precipitate (see p. 391), which subsides after some time. In order to test the sulphate of teroxide of bismuth (which is not decomposed by hydrochloric acid) in this manner, it must first be decomposed with *ammonia* in excess, and the precipitated teroxide having been dissolved in nitric or hydrochloric acid, the solution may be treated as above. This is an exceedingly delicate and characteristic test for bismuth.

AMMONIA; a white precipitate of *Hydrated Teroxide of Bismuth*; insoluble in excess; soluble in *dilute acids*.

CHROMATE OR BICHROMATE OF POTASSA; a yellow precipitate of *Chromate of Teroxide of Bismuth*, readily soluble in *dilute nitric acid*.

BLOWPIPE.—Solid compounds of bismuth, fused with *carbonate of soda*, on *charcoal*, in the *reducing flame*, yield a *Globule of Metal*, which is flattened by the first stroke of the hammer, but soon breaks in pieces, especially if slightly rubbed; a yellow incrustation of *Teroxide* appears on the charcoal.

OXIDE OF COPPER, CuO .

Solution best fitted for the reactions: Sulphate of Copper, $\text{CuO} \cdot \text{SO}_3$.

HYDROSULPHURIC ACID; a black precipitate of *Sulphide of Copper* (CuS); insoluble in *dilute sulphuric and hydrochloric acids*, even upon heating; readily soluble even in cold moderately *dilute nitric acid*, so that, in precipitating copper from a nitric solution by hydrosulphuric acid, it is requisite to dilute the solution very largely; soluble to a slight extent in *sulphide of ammonium*, but not in *sulphide of potassium*.

POTASSA; a blue precipitate of *Hydrated Oxide*, insoluble in excess; becomes black when heated in the liquid, being converted into *Anhydrous Oxide*. The presence of fixed organic matters (*sugar, tartaric acid, &c.*) causes this precipitate to redissolve in excess of potassa, with a *deep blue color*.

AMMONIA; a greenish-blue precipitate of a *basic salt*; readily soluble in ex-

cess, with a fine *blue color*, visible even when very minute quantities of copper are present.

FERROCYANIDE OF POTASSIUM; a brownish-red precipitate of *Ferrocyanide of Copper* ($\text{Cu}_2\text{C}_6\text{F}_6$); insoluble in *dilute acids*, readily soluble in *ammonia*; decomposed by *potassa*. This is the most delicate test for copper; before applying it, the solution should be acidified with *acetic acid* (strong mineral acids decompose the reagent; if these be present, an excess of *acetate of potassa* should be added to neutralize them); with very small quantities of copper, no precipitate is formed, but a pink color is imparted to the liquid.

IRON, or steel, perfectly clean, immersed in a solution of copper, slightly acidified with *sulphuric or hydrochloric acid*, becomes coated with a film of *Metallic Copper*, known by its color; this test enables us to detect very minute quantities of copper.

BLOWPIPE.—Solid compounds of copper, fused with *carbonate of soda* in the *reducing flame*, yield a mass of *Metallic Copper*, which may be fused into a very tough, red, *malleable* globule by long blowing; no incrustation is obtained; the operation is assisted by adding a little *cyanide of potassium*. When the quantity of copper present is so small that no globule can be obtained, it can often be detected by triturating the slag, with the surrounding parts of charcoal, in a small agate mortar, and levigating the powder till the lighter particles are washed away, when red spangles of copper become visible.

Compounds containing sulphur or arsenic should be well roasted in the *outer flame* before reduction, in order to volatilize these substances, which would injure the malleability of the metallic globule.

A small quantity of a compound of copper, fused with a *borax-bead* in the *outer flame* of the blowpipe, yields a *glass* which has a *greenish-blue color* when hot, and becomes *blue* on cooling; exposed to the *inner flame*, this glass either loses its color, or becomes tinged of an *opaque red*, according to the quantity of copper which is present.

OXIDE OF CADMIUM, CdO .

Solution best fitted for the reactions: Chloride of Cadmium, CdCl_2 .

HYDROSULPHURIC ACID; a bright yellow precipitate of *Sulphide of Cadmium* (CdS); insoluble in *alkaline sulphides*; insoluble only in cold, *very dilute sulphuric, hydrochloric, and nitric acids*; if the acid be only moderately dilute, the precipitate may dissolve, especially on heating; hence it is necessary to dilute acid solutions of cadmium very largely before treating with hydrosulphuric acid. In the presence of bisulphide of tin, it has been found that a considerable quantity of sulphide of cadmium may be left undissolved even by boiling dilute nitric acid.

AMMONIA; a white precipitate of *Hydrated Oxide of Cadmium*, very easily soluble in excess.

CARBONATE OF AMMONIA; a white precipitate of *Carbonate of Cadmium* (CdO.CO_2), slightly soluble in excess.

BLOWPIPE.—Solid compounds of cadmium, fused with *carbonate of soda*, in the *reducing flame*, give a characteristic *red-brown incrustation of oxide of cadmium* upon the *charcoal*, near the outer limit of the *oxidizing flame*.

TETROXIDE OF GOLD, Au_2O_3 .

Solution best fitted for the reactions: Tetrachloride of Gold, AuCl_4 .

HYDROSULPHURIC ACID; a black precipitate of *Tersulphide of Gold* (Au_2S_3); insoluble in *sulphuric, hydrochloric, or nitric acid*, alone (the latter, however, is

capable of oxidising the sulphur, leaving metallic gold), but soluble in a mixture of nitric and hydrochloric acids; soluble to a considerable extent in the alkaline sulphides.

OXALIC ACID; on boiling, a precipitate of finely divided *Metallic Gold*, appearing as a purple powder, which afterwards coheres in yellow flakes capable of assuming the *golden lustre* when rubbed; if a very small quantity of gold be present, the liquid only assumes a *purple* tinge. The presence of much free hydrochloric or nitric acid prevents the reduction; in such a case, ammonia may be added to the boiling solution, drop by drop, until the free acid is nearly neutralized.

SULPHATE OF OXIDE OF IRON also precipitates the gold as a *bluish-black powder*, becoming yellow and lustrous when rubbed; if the precipitate be very small, it may be collected upon a smooth filter, the latter washed, dried, and spread out upon a hard smooth surface; if the precipitate be then rubbed with a burnisher (of agate), the *lustrous spangles* will be visible.

CHLORIDE (SnCl) AND BICHLORIDE OF TIN (SnCl₂) (mixed); even in very dilute solutions of gold, a purple precipitate (*Purple of Cassius*, see p. 295), the tint of which varies according to the quantity of gold present; the precipitate is insoluble in *dilute acids*; the gold-solution should be first mixed with the bichloride of tin, and the chloride then added drop by drop. When the quantity of gold is extremely minute, a *pink tinge* pervades the solution.

A very delicate method of applying this test is as follows: *sesquichloride of iron* is added to chloride of tin (SnCl) until a permanent yellow color is produced, the solution is then considerably diluted; the gold-solution having likewise been much diluted, is poured into a beaker, which is placed on a sheet of white paper; a glass rod is dipped into the tin-iron-solution and afterwards into the gold-solution, when, if even a trace of the precious metal be present, a *blue or purple streak* will be observed in the track of the glass rod.

This purple of Cassius test has the advantage of being applicable even in very acid solutions.

BINOXIDE OF PLATINUM, PtO₂.

Solution best fitted for the reactions: Bichloride of Platinum, PtCl₂.

HYDROSULPHURIC ACID; black precipitate of *Bisulphide of Platinum (PtS₂)*; the precipitation is not complete in the cold; in order to remove platinum entirely from a solution, by hydrosulphuric acid, the liquid must be boiled after every saturation with the gas, until a specimen, filtered off, again saturated with hydrosulphuric acid, and boiled, gives no further precipitate. The bisulphide is insoluble in *dilute acids*, but dissolves to a great extent in *concentrated nitric acid*; it also dissolves, though with difficulty, in the *alkaline sulphides*.

CHLORIDE OF AMMONIUM; yellow crystalline precipitate of the *Double Chloride of Platinum and Ammonium (NH₄Cl.PtCl₂)*; soluble to some extent in water, insoluble in alcohol. In applying this test, the solution should be allowed to stand for about twelve hours, when very minute quantities of platinum may be detected by the formation of yellow crystals on the bottom and sides of the tube.

CHLORIDE OF TIN (SnCl) in presence of free hydrochloric acid, produces a dark brown-red color (due to the reduction of bichloride of platinum to the chloride); in exceedingly dilute solutions, the color is *yellow* and becomes darker on standing; the slightest traces of platinum are indicated by this test.

OXIDE OF TIN, SnO.

Solution best fitted for the reactions: Chloride of Tin, SnCl.

HYDROSULPHURIC ACID; dark brown precipitate of *Sulphide of Tin* (SnS); insoluble in cold *dilute acids*; converted by *boiling nitric acid* into insoluble *Binoxide of Tin*; insoluble in pure *alkaline sulphides*, but soluble, with the aid of heat, in *alkaline sulphides containing an excess of sulphur*, which converts the sulphide into *Bisulphide of Tin*; hence, the ordinary yellow sulphide of ammonium is capable of dissolving the sulphide of tin; if the solution be mixed with an excess of *hydrochloric acid*, the sulphide of ammonium is decomposed, and yellow bisulphide of tin precipitated.

CHLORIDE OF MERCURY (HgCl); at first, a white precipitate of *Subchloride* (often highly crystalline), which after a time, if a sufficient quantity of the tin-compound be present, is converted into a gray precipitate of *Metallic Mercury*. Since this reaction takes place even in highly dilute solutions, and in the presence of much free hydrochloric acid, it is very valuable for the detection of oxide of tin.

BLOWPIPE.—Solid compounds of tin, fused on *charcoal*, with *carbonate of soda* (or, very much more easily, with *cyanide of potassium*), in the *inner flame*, yield a *white malleable globule of Tin*, and a very slight white incrustation. Even if no globule be obtained, the spangles of tin are often visible after triturating and levigating the fused mass and surrounding particles of charcoal.

BINOXIDE OF TIN, SnO₂.

Solution best fitted for the reactions: Bichloride of Tin, SnCl₂.

HYDROSULPHURIC ACID; a bright yellow precipitate of *Bisulphide of Tin* (SnS₂); insoluble in *dilute sulphuric and hydrochloric acids*; converted into insoluble *Binoxide of Tin* by *boiling nitric acid*; soluble in a *mixture of hydrochloric and (a little) nitric acids*, with the aid of heat; soluble in *alkalies*, or in *alkaline sulphides*, and reprecipitated from the solution by acids.¹ When bisulphide of tin is added, by small portions, to *nitrate of potassa* in a state of fusion, it is rapidly oxidized; the fused mass, when treated with water, yields a solution which contains no tin, the whole of this metal being left in the residue; but if pieces of paper be also deflagrated with the nitre (as must always be the case when the precipitate is too small to be removed from the filter), the aqueous solution of the fused mass will contain a certain quantity of tin, which is, however, entirely precipitated on acidulating with nitric acid and boiling.

Bisulphide of tin, alone, is insoluble in a solution of *sesquicarbonate of ammonia*, even on gently heating, but when mixed with one of the sulphides of arsenic, it is dissolved to a considerable extent by the sesquicarbonate.

The color of bisulphide of tin is much impaired by admixture even of minute quantities of other sulphides.

SESQUICARBONATE OF AMMONIA; a white precipitate of *Hydrated Binoxide of Tin*;² redissolves to some extent in the cold, in an excess, but is completely reprecipitated on boiling. The presence of certain fixed organic matters (*tartaric acid, &c. g.*) prevents the precipitation.

CYANIDE OF POTASSIUM, fused with binoxide of tin in a covered porcelain

¹ Sulphide of ammonium does not extract quite the whole of the bisulphide of tin when mixed with the sulphide of mercury or cadmium, and extracts only a small part of it when mixed with sulphide of copper.

² This precipitate passes through the filter when washed with pure water, and should therefore be washed with solution of sesquicarbonate of ammonia.

crucible, reduces it to the metallic state; if the fused mass be heated with water, the cyanate of potassa is dissolved out, and the *particles of metal* subside; these, after decanting the supernatant liquid, may be heated to boiling with *concentrated hydrochloric acid*, and the presence of *Chloride of tin*, in the solution, proved by diluting with water and testing with *chloride of mercury*. By this method very small quantities of tin may be detected.

BLOWPIPE.—Compounds of the binoxide furnish the same result as those of the oxide (see p. 523) when examined before the blowpipe.

TEROXIDE OF ANTIMONY, SbO_2 .

Solution best fitted for the reactions: Terechloride of Antimony, $SbCl_3$.

(The solution of terechloride of antimony should not be diluted with pure water, but with water acidulated with hydrochloric acid.)

HYDROSULPHURIC ACID; an orange-red precipitate of *Tersulphide of Antimony* (SbS_3); insoluble in cold *dilute acids*; soluble in *moderately concentrated hydrochloric acid*, with evolution of hydrosulphuric acid; when boiled with *sibic acid*, partly dissolved, a white residue being left; the quantity dissolved increases with the dilution of the acid; soluble in *alkalies*, and in *alkaline sulphides*, and reprecipitated by *acids*, soluble to a very slight extent in *ammoniac carbonate of ammonia*, even on gentle heating.

WATER, added in large quantity to a solution of terechloride of antimony, not containing much free hydrochloric or tartaric acid, produces a white precipitate, which is an *Oxychloride*; this precipitate is distinguished from that furnished by bismuth under similar circumstances, by its solubility in *tartaric acid*.

POTASSA; a white precipitate of *Hydrated Teroxide of Antimony*, soluble in excess; if this solution be mixed with *nitrate of silver*, it gives a black precipitate of *Metallic Silver* (insoluble in *ammonia*), the teroxide of antimony being converted into antimonious acid.

The presence of *tartaric acid* prevents the precipitation by potassa.

SESQUICARBONATE OF AMMONIA; a white precipitate of *Hydrated Teroxide of Antimony*, soluble to a considerable extent in excess of the precipitant, especially on heating. The presence of tartaric acid prevents the precipitation.

METALLIC ZINC precipitates antimony from its solutions as a black powder.

If a solution containing antimony be introduced, through a funnel-tube, into an apparatus from which *hydrogen* is being evolved from *dilute sulphuric acid* by the action of *zinc*, the reduced antimony will combine with part of the nascent hydrogen, and will be evolved in the form of *Antimoniuretted Hydrogen gas* (SbH_3). If the gas be dried by passing through a tube, the anterior portion of which is loosely filled with cotton wool, and the remoter part with chloride of calcium, and be then allowed to escape from a tube of hard glass¹ drawn out to a fine point, the presence of antimony may be recognized by the following reactions:—

1. The gas will burn with a *bluish-green flame*, emitting white fumes of *Teroxide of Antimony*, which may be condensed in a cold beaker, dissolved in *hydrochloric acid*, and tested with *hydrosulphuric acid*.

2. If the inner surface of a porcelain capsule be depressed upon the flame, a *black spot* of metallic antimony will be deposited upon it, which is lustrous only when in thin layers; this coating of metal may be dissolved in *agua regia* and tested. (The operator should take care to prove, before commencing this experiment, that the flame of the hydrogen itself deposits no spot upon porcelain.)

¹ Hard glass should be used for all experiments of this description, because of the high temperature necessary, which would fuse ordinary English glass, and because the reduction of the lead contained in the latter might lead to error.

8. The glass tube from which the gas issues, should be heated with a spirit-lamp in the centre; a *lustrous mirror of antimony* will be deposited on the inside of the tube, immediately around the flame of the lamp, whilst the bluish-green tint of the hydrogen-flame in great measure disappears.

These reactions should be compared with those of arseniuretted hydrogen under similar circumstances.

If granulated zinc be boiled with a solution of antimony to which a very large excess of *potassa* has been added, the hydrogen which is evolved is free from antimoniretted hydrogen.

BLOWPIPE.—Solid compounds of antimony, when fused with *carbonate of soda*, on *charcoal*, in the *reducing flame*, yield a *globule* of metal, which volatilises if subjected for a considerable period to the action of the flame, and emits *white fumes* of teroxide; the globule is exceedingly *brittle*, and may be readily rubbed to a black powder. The charcoal becomes coated with a widely diffused *white incrustation*, which has a bluish appearance when in thin layers.

ANTIMONIC ACID, SbO_3 .

Solution best fitted for the reactions: Antimoniate of Potassa, KO.SbO_3 .

STRONG MINERAL ACIDS, especially *nitric*, produce a white precipitate of *Hydrated Antimonic Acid*, which redissolves to a great extent in excess of acid, particularly in *hydrochloric acid*.

HYDROSULPHURIC ACID, in a solution of an antimoniate, produces no precipitate, but if an excess of *hydrochloric acid* be previously added, an orange-red precipitate of *Pentasulphide of Antimony* (SbS_5), the behavior of which is similar to that of the tersulphide (see p. 524). It is necessary to state, in addition, that when pentasulphide of antimony is deflagrated with *nitre*, and the fused mass digested with water, almost the whole of the antimony remains in the residue.

POTASSA; no precipitate.¹ If to the solution containing excess of potassa, *nitrate of silver* be added, merely a brown precipitate of *Oxide of Silver* is obtained, which redissolves completely in excess of *ammonia* (see p. 524).

SESQUICARBONATE OF AMMONIA;² no precipitate.

Compounds of antimonic acid exhibit the same reactions with *zinc*, and before the *blowpipe*, as those of the teroxide of antimony.

ARSENIOUS ACID, AsO_3 .

Solution best fitted for the reactions: Arsenious Acid in saturated aqueous solution.

HYDROSULPHURIC ACID, in a pure solution of arsenious acid, a yellow color at first, and after a time, especially on heating, a yellow precipitate; if a little *hydrochloric acid* be added before the hydrosulphuric acid, the yellow precipitate of *Tersulphide of Arsenic* (As_2S_3) is obtained at once; insoluble in cold *dilute acids*, slightly soluble in *hydrochloric acid*, with the aid of heat, and readily so in *hot nitric acid*; soluble in *sesquicarbonate of ammonia*, especially on gently heating; very readily soluble in the *alkalies* and *alkaline sulphides*, and reprecipitated by *acids*. When deflagrated with *nitre*, the fused mass is entirely soluble in water, and *Arsenic Acid* may be detected in the solution.

When tersulphide of arsenic is fused with a large excess of *carbonate of soda*

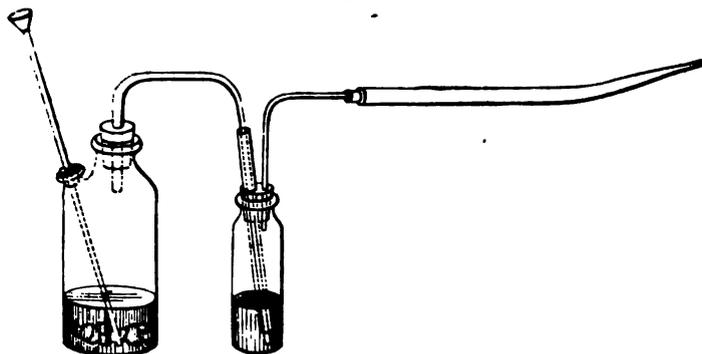
¹ This is strictly true in the case of antimoniate of potassa; but if this reagent be added to a hydrochloric solution of antimonic acid, a white precipitate is produced, which dissolves almost entirely in an excess of the precipitant.

² The same remark applies here as in the case of potassa.

and *cyanide of potassium*, the arsenic is reduced and volatilized, and if the operation be conducted in an apparatus so constructed that the vapors of arsenic may be preserved from contact with the air, and may be recondensed on a particular portion of the tube, the smallest quantities of arsenic may be thus detected. The test founded hereupon is known as that of *Fallesenius and Babo*, and requires a special description in this place, since it is now generally esteemed the safest test for arsenic in judicial investigations.

The apparatus consists of a small two-necked bottle for evolving carbonic acid, furnished with a funnel-tube, and an egress-tube for the gas, which is conducted into a small wash-bottle containing concentrated sulphuric acid, intended to dry the gas; from this wash-bottle, a second tube passes which is bent at right angles, and connected, by means of a cork, with the reduction-tube; this latter is made out of a piece of hard glass tube (combustion-tube) somewhat more than three-eighths of an inch in diameter, and drawn out at one extremity to a long open point; the length of the body of the tube should be about four inches, that of the point at least two and a half inches. The carbonic acid is evolved from pretty large fragments of marble (no powder), which are covered with water in the evolution-bottle into which dilute hydrochloric acid is poured through the funnel-tube.

Fig. 76.



A mixture of (as nearly as can be guessed) three parts of dry *carbonate of soda* and one part of *cyanide of potassium* is thoroughly dried in a porcelain capsule upon the sand-bath; one part of the arsenical sulphide (dried in the water-bath) is then intimately mixed, in a small (agate) mortar, with at least twelve parts of the above reducing mixture; the powder is placed in a strip of writing-paper folded so as to form a gutter, which is introduced into the body of the reduction-tube, so that the mixture may lay at about the centre; the tube is then turned half-round upon its axis, and the mixture allowed to fall upon the glass, when the gutter may be carefully withdrawn; the mixture should not occupy more than an inch in the tube; the latter is now connected with the carbonic acid apparatus, and the gas allowed to flow through it for some time; when it is certain that all air has been expelled, the evolution of carbonic acid is so moderated (by pouring water into the bottle) that only one bubble shall pass through the wash-bottle in a second; the reduction-tube is now heated throughout its whole length, by waving a spirit-lamp flame beneath it, until all the moisture is expelled; the spirit-lamp is then placed beneath the shoulder of the tube, and when this is well heated, a second spirit-lamp is applied, to heat the mixture, commencing at the posterior part; when the whole of the mixture has been heated, the experiment may be concluded by directing a blowpipe-flame upon that portion of the tube, until the mass is completely fused; the vapors of

metallic arsenic are carried forward by the stream of carbonic acid, and, since the shoulder of the tube is heated, they pass on and condense in the narrow point, where they form a *lustrous mirror* of about an inch in length; a distinct *garlic odor* is also perceived at the point of the tube throughout the experiment. When the quantity of arsenic is exceedingly minute, merely a *thin gray film* is deposited, which is only visible against a piece of white paper.

The portion of the point which contains the metallic arsenic may be cut off with a sharp file, and the metal dissolved off with a few drops of *concentrated nitric acid*, the solution carefully evaporated till the excess of acid is expelled, water added, and the solution tested with *nitrate of silver*, and, if necessary, *dilute ammonia* added, drop by drop, when the brick-red precipitate of *Arseniate of Silver* (see p. 530) will be obtained.

This test of Fresenius and Babo possesses advantages which entitle it to a preference over all other tests for arsenic hitherto discovered; for, 1. It can be applied to the very smallest quantities of material: 2. Its results depend very little upon the skill or judgment of the operator; and, 3. It cannot lead us to mistake any other metal for arsenic; antimony, which so much resembles arsenic in many of its reactions, does not respond to this test. It is true that mercury compounds, when treated in this way, would yield a metallic sublimate, but this differs widely from that of arsenic, and other reactions would invariably prevent any mistake arising from this cause.

NITRATE OF SILVER does not produce a precipitate in an aqueous solution of arsenious acid, but if *ammonia* be gradually added, a yellow precipitate of *Arsenite of Silver* ($2\text{AgO} \cdot \text{AsO}_2$) is obtained; readily soluble in *ammonia* and in *nitric acid*; great care is necessary in neutralizing with ammonia, which should be very dilute, and added, drop by drop, with frequent agitation; if too much ammonia has been added, the precipitate may frequently be obtained by gently evaporating the solution upon a water-bath (all sulphuretted hydrogen being excluded); it is also a good plan to neutralize the solution before adding the nitrate of silver, by rendering it slightly alkaline with *ammonia*, and then evaporating on a water-bath till the excess of the latter is expelled.

The application of nitrate of silver as a test for arsenious acid is, however, very limited, because so many substances (especially chlorides) interfere with the reaction.

SULPHATE OF COPPER produces no precipitate in a solution of arsenious acid, but if *ammonia* be carefully added, a yellowish-green precipitate of *Arsenite of Copper* ($2\text{CuO} \cdot \text{AsO}_2$, *Scheele's Green*) is obtained; soluble in *nitric acid* and in *ammonia*: the same remarks apply to this as to the preceding test.

If *sulphate of copper*, in small proportion, be added to a solution of arsenious acid, afterwards *potassa* in excess, and the solution boiled, a red precipitate of *Suboxide of Copper* (Cu_2O) is obtained, the arsenious acid being converted into *arsenic acid*; this test is only useful for distinguishing between arsenious and arsenic acids, and would be valueless as a test for arsenic, since many other substances (e. g. sugar) are capable of producing the same effect.

REINSCH'S TEST.—Clean *copper*, boiled in a *hydrochloric* solution, containing arsenic, becomes coated with a *steel-gray film* of the metal, which, if the quantity be sufficient, will separate, after long boiling, in *large black scales*. This is a very delicate test for arsenic, and since it is more readily applied than any other, we shall consider it in detail, as it is often used in medico-legal analyses.

The solution to be tested, which may contain organic matters, but should be pretty free from *oxidizing agents* (*nitric and chloric acids, &c.*) and not very thick, is mixed with sufficient *hydrochloric acid* to render it very distinctly acid, and boiled with several pieces of *copper wire* (cleaned with *concentrated nitric acid*, and washed) about an inch long, for two or three minutes; if they are not then coated, the boiling may be continued for about ten minutes; but if a film

is deposited upon, them at first, they should be withdrawn, lest it may scale off; the slips are then well washed with *water*, and carefully dried, either by pressure between blotting-paper, or better, in a water-bath; they are afterwards introduced into a tube of hard glass, about $\frac{1}{2}$ inch in diameter, and so constricted as to admit of the passage of only a feeble current of air; this tube is heated gradually, in an oblique position, over a spirit-lamp, when a *sublimate of shining crystals of Arsenious Acid* will be formed in the cool part of the tube; if these be examined with a magnifier, it will be seen that they are octohedra, like crystals of alum; the portion of glass upon which these crystals are deposited may be cut off, boiled for some seconds with *water*, and the solution examined for arsenious acid, especial recourse being had to the tests with *hydrochloric* and *hydrosulphuric acids*, and with *nitrate of silver*.

In careful hands, this test leads to a very safe conclusion as to the presence or absence of arsenic, since, though many other metals may be deposited upon the copper, none but arsenic will yield a crystalline sublimate; this test, however, is generally regarded as merely a trial test, so that if it should give no indication whatever of the presence of arsenic, it is not considered necessary to proceed any further.

MARSH'S TEST.—If a solution of arsenic be poured into an apparatus (*b, a, c*) from which *hydrogen* is evolved by the action of *zinc* upon *water* in the presence of *sulphuric acid*, *Arseniretted Hydrogen* (AsH_3) is produced; the gas should be dried by passing through a tube (*d*), which is half filled (at the end nearest to the evolution-bottle) with *cotton-wool*, and half with fragments of *chloride of calcium*, and may be recognized by the following experiments.

Fig. 77.



1. The gas is allowed to escape from a tube of hard glass (*e*) about six inches long, drawn out so as to form a jet at its extremity, where the gas may be kindled; it burns with a *livid blue flame*, producing *Arsenious Acid*, which may be condensed in a cold beaker, dissolved in *hot water*, and tested (especially with *nitrate of silver*, and with *hydrochloric* and *hydrosulphuric acids*).

2. By depressing the inner surface of a porcelain capsule upon the flame, a *black* (generally) *lustrous spot of metallic arsenic* is obtained (this experiment should always be tried with the hydrogen-flame before the arsenical solution is poured into the evolution-bottle);¹ this spot may be tested by dissolving in *concentrated nitric acid*, evaporating just to dryness upon a sand-bath, adding *water*, and afterwards *nitrate of silver*, with, if necessary, a little *dilute ammonia*, when a brick-red precipitate of *Arseniate of Silver* will be obtained; an antimony

¹ The porcelain should not be allowed to remain in the flame for more than a second or two, since the minute spots would be dispelled if the porcelain were to become very hot.

spot, when treated in this way, generally gives a slight dirty-white precipitate with nitrate of silver.

The incrustation of arsenic (whether on a porcelain surface or in a glass tube) may be dissolved by solution of *chloride of lime*, which does not affect the antimony-incrustation: this test may serve, to some extent, to distinguish the two metals, but is not adequate to the detection of traces of antimony in a mirror of arsenic.

3. The centre of the tube (*g*) through which the gas passes may be heated with a spirit-lamp (*f*), when the arseniuretted hydrogen is decomposed, a *mirror of metallic arsenic* being deposited, while the hydrogen-flame regains, in great measure, its natural color; the mirror in this case, in consequence of its greater volatility, is not deposited immediately in the vicinity of the spirit-lamp, but at a considerable distance beyond the heated part of the tube; if this portion of the tube be cut off, and gently heated, the peculiar *garlic odor* will be perceptible; the crust of arsenic may also be tested in the same way as that obtained in the porcelain capsule (*see* 2).

Although this test enables us to detect very small quantities of arsenic, it is not now generally recommended, in consequence of the danger of confounding antimony with arsenic; of course, in a mixture of the two, it would be impossible to distinguish either with certainty.

Marsh's test, however, may afford a very satisfactory proof of the *absence* of both these metals.¹

FLEITMANN'S TEST.—If a solution containing arsenic be mixed with a large excess of a *concentrated solution of potassa*, and boiled with fragments of *granulated zinc*, arseniuretted hydrogen is evolved, and may be easily recognized by allowing it to pass on to a piece of filter-paper spotted over with solution of *nitrate of silver*; these spots assume a *purplish-black color*, even when a small quantity of arsenic is present. This experiment may be performed in a small flask, furnished with a perforated cork carrying a piece of glass tube of about $\frac{1}{4}$ -inch diameter. It will be observed that this test serves to distinguish arsenic from antimony.

Solid compounds containing arsenic, mixed with *carbonate of soda* and *charcoal* (*black flux*, or a mixture of equal parts of *wood-charcoal* and *carbonate of soda*, previously ignited in a covered crucible), and heated in a tube of hard glass, expanded into a bulb at one extremity, and thoroughly dried, yield a *black lustrous ring of metallic arsenic* upon the cool part of the tube.

BLOWPIPE.—Solid compounds containing arsenic, when heated to redness, on *charcoal*, in the *reducing flame*, emit a characteristic *garlic odor*, probably due to an oxide of arsenic inferior to arsenious acid.

ARSENIC ACID, As_2O_3 .

Solution best fitted for the reactions: Arsenic acid in aqueous solution.

HYDROSULPHURIC ACID does not produce an immediate precipitate in solution of arsenic acid, even when mixed with *hydrochloric acid*, but if the solution be heated to boiling, or allowed to stand for some time, a yellow precipitate of *Pentasulphide of Arsenic* (As_2S_5) is obtained, which exhibits the same characters as the tersulphide. The complete removal of arsenic acid from a solution by means of sulphuretted hydrogen, is attended with some difficulty; it is necessary repeatedly to saturate it with the gas, and to boil after each saturation; it is better, however, to convert the *arsenic acid* into *arsenious acid*, by saturating the

¹ A great obstacle to the employment of Marsh's test is the difficulty of obtaining zinc and sulphuric acid perfectly free from arsenic, for which they should be very carefully tested previous to use.

liquid with *sulphurous acid*, and subsequently boiling until the excess of the latter is expelled, which may be known by the disappearance of the odor. The arsenic may then readily be precipitated by *hydrosulphuric acid*.

NITRATE OF SILVER; a brick-red precipitate of *Arsenate of Silver* ($3\text{AgO} \cdot \text{AsO}_5$); readily soluble in *nitric acid* and in *ammonia*; if it should be required to apply this test to a solution containing *free nitric acid*, the latter may be neutralized with *ammonia*, and the excess of ammonia expelled by evaporation; if chlorides be present, the solution may be acidulated with *nitric acid*, the whole of the chlorine precipitated by *nitrate of silver*; the clear fluid containing excess of that reagent is then very carefully neutralized with *dilute ammonia*, when the brick-red precipitate makes its appearance; it is a good plan to pour the dilute ammonia very gradually upon the surface of the acid liquid, so as to form two distinct layers, at the junction of which a brown line of *Arsenate of Silver* may be seen.

In those reactions which depend upon the reduction of the arsenic to the metallic state, arsenic acid resembles the arsenious.

§ 339. FIFTH GROUP.

Metallic oxides, the chlorides corresponding to which are insoluble or sparingly soluble in water and dilute hydrochloric acid.

OXIDE OF SILVER (AgO), SUBOXIDE OF MERCURY (Hg_2O), OXIDE OF LEAD (PbO).

OXIDE OF SILVER, AgO .

Solution best fitted for the reactions: Nitrate of Silver, $\text{AgO} \cdot \text{NO}_3$.

HYDROCHLORIC ACID; a white precipitate of *Chloride of Silver* (AgCl), which becomes violet when exposed to light; insoluble in *water* and in *nitric acid*, readily soluble in *ammonia*. When this precipitate is mixed with a certain quantity of subchloride of mercury, it no longer darkens when exposed to light.

SOLUBLE CHLORIDES affect silver salts like hydrochloric acid.

BLOWPIPE.—Solid compounds of silver, fused with *carbonate of soda*, on *charcoal*, before the blowpipe, yield a *globule* of white, *malleable metal*, without incrustation of the charcoal support.

SUBOXIDE OF MERCURY, Hg_2O .

Solution best fitted for the reactions: Nitrate of Suboxide of Mercury, $\text{Hg}_2\text{O} \cdot \text{NO}_3$.

HYDROCHLORIC ACID: a white (slightly yellowish in large masses) precipitate of *Subchloride of Mercury*, Hg_2Cl_2 ; insoluble in *water* and in *cold hydrochloric and nitric acids*; blackened by *ammonia*, being converted into the *Suboxide*, which is not soluble in *ammonia*.

The reactions which depend upon the reduction of mercury to the metallic state, are exhibited also by the oxide of mercury, and have been described in the section containing the reactions of that oxide (see p. 519).

OXIDE OF LEAD, PbO .

Solution best fitted for the reactions: Nitrate of Lead, $\text{PbO} \cdot \text{NO}_3$.

HYDROCHLORIC ACID in moderately concentrated solutions, a white precipitate of *Chloride of Lead*, PbCl_2 , soluble in much *acid water*, and therefore not

produced in dilute solutions; dissolves pretty readily in *boiling water*, and is deposited in fine needles as the solution cools; is not dissolved by *ammonia*.

DILUTE SULPHURIC ACID; in very dilute solutions, only after standing for some time a white, heavy precipitate of *Sulphate of Lead* ($\text{PbO}.\text{SO}_3$); very slightly soluble in water and in *dilute nitric acid*; soluble in *hot hydrochloric acid*, and in *potassa*. This reaction with sulphuric acid serves to distinguish the oxide of lead from all other oxides, except baryta and strontia.

HYDROSULPHURIC ACID; a black precipitate of *Sulphide of Lead* (PbS);¹ insoluble in water, and in *cold dilute acids*; almost entirely dissolved by *hot dilute nitric acid*, as nitrate of lead, a residue of sulphur with a little sulphate of lead being left; *concentrated nitric acid* converts it into sulphate, which is left undissolved.

POTASSA; a white precipitate of *Hydrated Oxide of Lead*, readily soluble in an excess.

AMMONIA; a white precipitate of *Hydrated Oxide of Lead*, insoluble in excess;² readily soluble in *dilute nitric acid*. Solution of acetate of lead does not give any precipitate immediately, with ammonia, but the solution, after some time, deposits a *basic salt* of oxide of lead.

CHROMATE or BICHROMATE OF POTASSA; a yellow precipitate of *Chromate of Lead* ($\text{PbO}.\text{CrO}_3$); insoluble in water and in *acetic acid*; sparingly soluble in *dilute nitric acid*; readily soluble in *potassa*.

BLOWPIPE.—Solid compounds of lead, when fused with *carbonate of soda* on *charcoal*, in the *inner blowpipe-flame*, furnish a very soft *malleable globule of metal*, which marks paper like a pencil; the charcoal around the *oxidizing flame* becomes covered with a yellow (or brownish) incrustation of *oxide of lead*.

REACTIONS OF THE ACIDS.

§ 340. In considering the reactions of the acids, we shall divide them into *inorganic* and *organic* acids, restricting the latter designation to those which, when heated (either alone or in combination), are either *blackened*, from separation of carbon, or evolve inflammable gases, so that they appear to *burn with flame* when heated upon platinum. Among the inorganic acids we are compelled to place *oxalic acid* (although it is, strictly speaking, an organic acid), since its compounds usually exhibit none of the ordinary appearances which are taken as indications of the presence of organic acids. The acids of cyanogen are, for a similar reason, included in this class.

The following acids are of sufficient importance to be studied in this work:—

Inorganic:³ Sulphuric, phosphoric, boracic, silicic, sulphurous, chromic, hydrofluoric, carbonic, oxalic, hydrochloric, hydrobromic, hydriodic, hydrosulphuric, hydrocyanic, hydrosulphocyanic, hydroferrocyanic, hydroferricyanic, nitric, chloric, and hypochlorous.

Organic:⁴ Tartaric, tannic, gallic, citric, uric, benzoic, succinic, acetic.

¹ If much free hydrochloric acid be present, this precipitate is at first of a red color (see p. 479), becoming black only after some time.

² In presence of ammoniacal salts, however, this precipitate is redissolved to some extent by an excess of ammonia; so that if a solution of nitrate of lead, mixed with a large excess of free nitric acid, be decomposed with a large excess of ammonia, a considerable quantity of lead may be found in the filtered solution.

³ Arsenious and arsenic acids have been already considered.

⁴ The history of the organic acids will be given in a subsequent part of this work.

INORGANIC ACIDS.

The inorganic acids are, for the convenience of study, divided into three groups, according to their behavior with reagents.

The *first group* includes those acids which are precipitated from the solutions of their neutral salts by chloride of barium—viz: sulphuric, phosphoric, boracic, silicic, sulphurous, chromic, hydrofluoric, carbonic, and oxalic acids.

The acids contained in the *second group* are such as are precipitated by nitrate of silver from solutions slightly acidified with nitric acid; these are hydrochloric, hydrobromic, hydriodic, hydrosulphuric, hydrocyanic, hydrosulphocyanic, hydroferrocyanic, and hydroferricyanic acids.

In the *third group* we find those acids which we are not able to precipitate from their solutions, in consequence of the solubility of all their compounds; they are nitric, chloric, and hypochlorous acids.

§ 341. FIRST GROUP.

Acids precipitated from solutions of their neutral salts by chloride of barium.

FIRST SECTION. *Acids which are not affected when heated (either alone or in combination) with concentrated sulphuric acid.*

SULPHURIC ACID (SO_2)	PHOSPHORIC ACID (PO_2)
BORACIC ACID (BO_2)	SILICIC ACID (SiO_2)

SULPHURIC ACID.

Solution best fitted for the reactions: Sulphate of Magnesia, $\text{MgO} \cdot \text{SO}_2$.

CHLORIDE OF BARIUM; in neutral, acid, or alkaline solutions, a white precipitate of *Sulphate of Baryta* ($\text{BaO} \cdot \text{SO}_2$), soluble to a very slight extent in *hot hydrochloric acid*. In strongly acid solutions the precipitate is not formed immediately. When this test is to be applied in solutions containing much free hydrochloric or nitric acid, they should first be largely diluted, lest a precipitate of chloride of barium or nitrate of baryta should be formed, since these salts are sparingly soluble in strongly acid liquids.

CHLORIDE OF CALCIUM; in concentrated solutions, a white precipitate of *Sulphate of Lime* ($\text{CaO} \cdot \text{SO}_2$); insoluble in *acetic acid*; soluble in much water; soluble in *hot hydrochloric acid*.

BLOWPIPE.—Solid sulphates, fused on platinum wire with a *mixture of carbonate of soda and charcoal*—in the *reducing flame*, yield a bead containing *Sulphide of Sodium* (NaS); if this bead be placed upon a clean piece of *silver*, and moistened with *dilute hydrochloric acid*, *Hydrosulphuric Acid* is evolved, and produces a *black stain* (AgS) upon the metal. In this test, the carbonate of soda must, of course, be free from sulphate.

Any compound of sulphur will exhibit this reaction.

PHOSPHORIC ACID.

(We shall confine our attention here merely to common phosphoric acid ($3\text{HO} \cdot \text{PO}_2$), since the pyro and meta-phosphoric acids are of much less frequent occurrence, and their reactions have been described in the former part of this work).

Solution best fitted for the reactions: Phosphate of Soda, $2\text{NaO} \cdot \text{HO} \cdot \text{PO}_3$.

CHLORIDE OF BARIUM; in neutral or alkaline solutions, a white precipitate of *Phosphate of Baryta* ($2\text{BaO} \cdot \text{HO} \cdot \text{PO}_3$); readily soluble in *hydrochloric acid*, and reprecipitated by *ammonia*.

CHLORIDE OF CALCIUM, in neutral or alkaline solutions, a white precipitate of *Phosphate of Lime* ($2\text{CaO} \cdot \text{HO} \cdot \text{PO}_3$); soluble in *acetic* or *hydrochloric acid*, and reprecipitated by *ammonia*.

NITRATE OF SILVER, in neutral or very slightly alkaline solutions, a yellow precipitate of *Tribasic Phosphate of Silver* ($3\text{AgO} \cdot \text{PO}_3$); soluble in *nitric acid* or in *ammonia*.

SESQUICHLORIDE OF IRON, in neutral or slightly alkaline solutions, or in solutions containing free *acetic acid*, a yellowish-white gelatinous precipitate of *Phosphate of Sesquioxide of Iron* ($\text{Fe}_2\text{O}_3 \cdot \text{PO}_3$), insoluble in *acetic acid*; soluble to some extent in solution of *acetate of sesquioxide of iron*; readily soluble in the *mineral acids*; decomposed by *alkalies*; completely decomposed by boiling with *sulphide of ammonium*, sulphide of iron being left, and phosphate of ammonia remaining in solution.

TARTARIC ACID and other fixed organic matters prevent the precipitation of phosphate of sesquioxide of iron.

In applying this test to the solution of a phosphate (e.g. phosphate of lime) in *hydrochloric* (or any other mineral) *acid*, it is requisite to replace the latter by *acetic acid*, which may be effected by the addition of an excess of *acetate of potassa*; sesquichloride of iron should then be cautiously added; the first drop will produce a precipitate if any notable amount of phosphoric acid be present; in order to separate all the phosphoric acid from the solution, sesquichloride of iron must be added until, after the subsidence of the precipitate, the supernatant liquid has a red tint, due to the acetate of sesquioxide of iron, which may hold in solution a little of the phosphate; in order to precipitate the latter, the solution (with the suspended precipitate) must be boiled for a minute or two, when the acetate of sesquioxide of iron is decomposed, with separation of a basic acetate, which is precipitated together with the phosphate;¹ for the detection of the phosphoric acid in the mixed precipitate of phosphate and basic acetate of sesquioxide of iron, this is collected on a filter, washed and dissolved off the filter with *warm dilute hydrochloric acid*; the solution is mixed with excess of *ammonia* and *sulphide of ammonium*, boiled and filtered off from the sulphide of iron; the filtrate is concentrated by evaporation, again filtered, if necessary, from a little separated sulphur, and tested for phosphoric acid with a *mixture of chloride of ammonium, ammonia and sulphate of magnesia*, as described below.

A *mixture of CHLORIDE OF AMMONIUM, AMMONIA, and SULPHATE OF MAGNESIA*, gives a white, highly crystalline precipitate of *Phosphate of Magnesia and Oxide of Ammonium* ($2\text{MgO} \cdot \text{NH}_3 \cdot \text{O} \cdot \text{PO}_3$); somewhat soluble in water, less soluble in solution of *ammonia*, readily soluble in *acids*. In dilute solutions this precipitate is formed only after some time; the solution should be violently agitated. Care must be taken that sufficient chloride of ammonium is present to prevent the precipitation of hydrate of magnesia. This test should not be applied to solutions containing tartaric acid, since a mixture of that acid with chloride of ammonium, ammonia, and sulphate of magnesia, deposits a crystalline precipitate after a time. The application of this test is unfortunately restricted to those phosphates which are soluble in water, since the free ammonia (necessary to its success) would precipitate unchanged any phosphate which had been dissolved in an acid.

¹ The solution filtered off from this precipitate will be colorless (or very nearly so) if the operation is successful.

MOLYBDATE OF AMMONIA; even in solutions containing free nitric acid, a yellow precipitate (see p. 447), which is most evident when a small quantity of phosphoric acid is present. This test is especially adapted for the detection of minute quantities of phosphoric acid in a nitric solution of phosphate of alumina, phosphate of lime, &c.

BORACIC ACID.

Solution best fitted for the reactions: Biborate of Soda, $\text{NaO} \cdot 2\text{BO}_2$.

CHLORIDE OF BARIUM, in neutral and alkaline solutions, a white precipitate of *Borate of Baryta* ($\text{BaO} \cdot \text{BO}_2$), soluble in *hydrochloric acid*. Since borate of baryta is soluble to some extent in *ammoniacal salts*, no precipitate is produced, if these be present in sufficient quantity; for the same reason, when borate of baryta is dissolved in a large excess of hydrochloric acid, *ammonia* does not reprecipitate it.

CHLORIDE OF CALCIUM; in neutral and alkaline solutions, a white precipitate of *Borate of Lime* ($\text{CaO} \cdot \text{BO}_2$), soluble in *acetic acid*; this precipitate is also dissolved by *ammoniacal salts*.

NITRATE OF SILVER; a white precipitate of *Borate of Silver* ($\text{AgO} \cdot \text{BO}_2$), soluble in *nitric acid* and in *ammonia*.

If a solution containing boracic acid be mixed with about half its volume of *concentrated sulphuric acid*, an equal volume of *alcohol* (or *naphtha*) added, and the mixture kindled, it will burn with a fine *green flame*; the mixture should be well stirred whilst burning, and should be allowed to burn out before the absence of boracic acid is inferred from the non-appearance of the green flame. The presence of copper (which might also color the flame) is to be avoided in this experiment.

SILICIC ACID.

Solution best fitted for the reactions: Silicate of Potassa, $\text{KO} \cdot \text{SiO}_2$.

CHLORIDE OF BARIUM; in neutral and alkaline solutions, a white precipitate of *Silicate of Baryta* ($\text{BaO} \cdot \text{SiO}_2$), soluble (entirely, or in great measure) in *hydrochloric acid*.

CHLORIDE OF CALCIUM; a similar reaction.

HYDROCHLORIC ACID; in pretty concentrated solutions, a gelatinous white precipitate of *Hydrated Silicic Acid*; soluble, entirely, or, in great measure, in excess, and reprecipitated by excess of *ammonia*. If the hydrochloric solution be evaporated to dryness, and the residue heated with hydrochloric acid, the whole of the silicic acid will be left undissolved in the form of white flakes.

NITRIC ACID acts in a similar manner, but does not readily redissolve the gelatinous silicic acid which is precipitated at first.

Insoluble silicic acid (quartz, sand, &c.), when fused, on platinum foil, with **CARBONATE OF POTASSA OR SODA** (3 or 4 parts), expels the carbonic acid, forming an *alkaline silicate*, which dissolves entirely (or nearly so) in water; for the complete success of this experiment, the silica must be reduced to an impalpable powder.

BLOWPIPE.—If a bead of *carbonate of soda* be made upon a loop of platinum wire, and, having been dipped, while hot, into powdered silicic acid, be again fused in the hottest part of the blowpipe flame, a point will be attained, in repeating this operation, when the bead remains *transparent on cooling* (whereas the bead of pure carbonate of soda becomes *opaque*); this is a very characteristic reaction of silicic acid; the bead is usually of a yellowish color, from the presence of a little iron.

§ 342. SECOND SECTION OF THE FIRST GROUP. *Acids which are decomposed*

or expelled when heated (either alone or in combination) with concentrated sulphuric acid.



SULPHUROUS ACID.

Solution best fitted for the reactions: Sulphite of Oxide of Ammonium,
 $\text{NH}_4\text{O.SO}_2$.

Solid sulphites (sulphite of soda, *e. g.*), heated with CONCENTRATED SULPHURIC ACID, are decomposed with effervescence, *Sulphurous Acid* being evolved, which may be recognized by its characteristic odor of burning sulphur.

HYDROCHLORIC ACID also evolves sulphurous acid from its salts; the decomposition is attended with *effervescence* (especially on heating) if the solution be not too dilute. When there is any doubt respecting the odor, it may often be set at rest by conducting the gas (through a bent tube) into a saturated solution of *sulphuretted hydrogen*, in which sulphurous acid would cause a separation of *Sulphur* (it must be remembered that oxidizing agents, chlorine, for example, would have the same effect).

CHLORIDE OF BARIUM; in neutral and alkaline solutions, a white precipitate of *Sulphite of Baryta* (BaO.SO_2) soluble in *hydrochloric acid*; from this solution (provided it be first boiled to expel the sulphurous acid) *ammonia* does not reprecipitate the sulphite. If the hydrochloric solution of sulphite of baryta be boiled with a few drops of *concentrated nitric acid*, a precipitate of *Sulphate of Baryta* is formed; this precipitate should be heated with a considerable quantity of water, lest any nitrate of baryta should have been thrown down.

CHLORIDE OF CALCIUM; in neutral and alkaline solutions, a white precipitate of *Sulphite of Lime* (CaO.SO_2) soluble in *hydrochloric acid*.

NITRATE OF SILVER, a white precipitate of *Sulphite of Silver* (AgO.SO_2) which becomes dark gray when heated in the liquid, being decomposed into *Sulphuric Acid* and *Metallic Silver*.

The sulphites, when fused with *carbonate of soda* and *charcoal*, exhibit the same behavior as the sulphates (*see p. 532*).

CHROMIC ACID.

Solution best fitted for the reactions: Chromate of Potassa, KO.CrO_2 .

Solid chromates, when heated with CONCENTRATED SULPHURIC ACID evolve *Oxygen*, which may be recognized by means of a semi-extinguished match; *Sulphate of Sesquioxide of Chromium* remains in the solution (*see p. 331*).

Chloride of barium, in neutral and alkaline solutions; a yellow precipitate of *Chromate of Baryta* (BaO.CrO_2), soluble in *hydrochloric acid*, and reprecipitated by *ammonia*.

NITRATE OF SILVER, a purple-red precipitate of *Chromate of Silver* (AgO.CrO_2) soluble in *nitric acid* and in *ammonia*.

ACETATE OF LEAD; a yellow precipitate of *Chromate of Lead* (PbO.CrO_2) insoluble in *acetic acid*.

HYDROSULPHURIC ACID; in neutral and alkaline solutions, a greenish-gray precipitate of *Sesquioxide of Chromium* mixed with *Sulphur* (*see p. 332*); if *hydrochloric acid* be added before hydrosulphuric acid, only sulphur will be precipitated, while sesquichloride of chromium will be found in the (*green*) solution.

SULPHUROUS ACID, added to an acid solution, reduces the chromic acid to the state of (*Sulphate of*) *Sesquioxide of Chromium* ($\text{Cr}_2\text{O}_3.3\text{SO}_2$).

When a solution containing chromic acid is heated with an excess of *hydrochloric acid* and a little *alcohol*, the chromic acid is converted into *sesquichloride of chromium* (Cr_2Cl_6).

HYDROFLUORIC ACID.¹

Solution best fitted for the reactions : Fluoride of Potassium, KF.

When solid fluorides (fluoride of calcium) are heated with CONCENTRATED SULPHURIC ACID, *Hydrofluoric Acid* is evolved, and may be recognized by its *pungent odor*, by the *thick fumes* which it produces in *moist air*, and by its property of *corroding glass*.

If the experiment be made in a test-tube, the sides of the latter will suffer considerable corrosion, which will not be perceived, however, until the tube is washed and dried.

It is much better to perform the experiment in a platinum crucible; the powdered fluoride should be placed in the latter, a quantity of concentrated sulphuric acid poured over it, and the mouth of the crucible covered with a smooth glass plate; if the crucible be now gently heated on a sand-bath for half an hour, the glass plate will be found more or less deeply etched.

If a very small quantity of a fluoride is to be tested, it may be placed in a watch-glass, an excess of concentrated sulphuric acid added, and the mixture dried upon a sand-bath; if the mass be then washed off the glass, and the latter dried, the corrosion will become apparent.

Neither of these tests, however, can be applied when the compound contains silicic acid, since the nascent hydrofluoric acid would more readily act upon this than upon the glass; the following test must then be employed.

If a solid fluoride be mixed with *sand*, and heated with *concentrated sulphuric acid*, *Tetrafluoride of Silicon* is evolved, which may be recognized by its depositing a *coating of Silicic Acid upon moist surfaces* (see p. 220). For this experiment, a test-tube or small flask is employed, furnished with a perforated cork carrying a straight piece of glass tube, about $\frac{1}{4}$ inch in diameter, and 6 inches long; this tube is wetted internally with a little water, without wetting the cork; if the mixture of the fluoride with sand and sulphuric acid be heated in the (well-dried) flask, the tetrafluoride of silicon is evolved, and deposits a white coating of silica upon the walls of the tube.

If this experiment be carefully performed, it enables us to detect very small quantities of fluorine.

CHLORIDE OF BARIUM; in neutral and alkaline solutions, a white precipitate of *Fluoride of Barium* (BaF) soluble in *hydrochloric acid*, and reprecipitated by *ammonia*.

CHLORIDE OF CALCIUM; in neutral and alkaline solutions, a white precipitate of *Fluoride of Calcium* (CaF), insoluble, or nearly so, in *acetic acid*; soluble to some extent in *hydrochloric acid*, and reprecipitated by *ammonia*.

Insoluble fluorides (fluoride of calcium) when finely powdered and fused with 3 or 4 parts of *carbonate of potassa and soda*, yield a mass from which water extracts the *Alkaline Fluoride*, which may be detected by adding a slight excess of *acetic acid*, and *chloride of calcium*.

CARBONIC ACID.

Solution best fitted for the reactions : Carbonate of Soda, NaO.CO_2 .

Solid carbonates (carbonate of lime) are decomposed, even in the cold, by

¹ The fluorides are considered as *compounds of hydrofluoric acid*, because, although they really do not contain this acid, they are produced whenever hydrofluoric acid comes in contact with bases.

CONCENTRATED SULPHURIC ACID, *Carbonic Acid* being evolved, with violent *effervescence*.

HYDROCHLORIC ACID also expels the carbonic acid with *effervescence*; this is taken advantage of in testing for carbonic acid; the substance is treated with hydrochloric acid in a test-tube, and the evolved gas immediately decanted into another test-tube half filled with *baryta-water*; the *Carbonate of Baryta* is formed as a crust upon the surface of the liquid, and upon agitating the latter, it absorbs the rest of the carbonic acid in the tube, and becomes *turbid*.

CHLORIDE OF BARIUM; a white precipitate of *Carbonate of Baryta* (BaO.CO_2), readily soluble in *hydrochloric acid*, and, provided the solution be gently heated to expel the carbonic acid, not reprecipitated by *ammonia*.

CHLORIDE OF CALCIUM; a white precipitate of *Carbonate of Lime* (CaO.CO_2) soluble in *acetic acid*.

NITRATE OF SILVER; a white precipitate of *Carbonate of Silver* (AgO.CO_2), soluble in *nitric acid* and in *ammonia*.

OXALIC ACID.

Solution best fitted for the reactions: Oxalate of oxide of ammonium, $\text{NH}_4\text{O}\bar{\text{O}}$.

Oxalic acid, or an oxalate, in the solid state, heated with CONCENTRATED SULPHURIC ACID, yields *Carbonic Oxide*, together with *Carbonic Acid* (see p. 196), which are evolved with effervescence; if the mouth of the test-tube be approached to a flame, the carbonic oxide takes fire, and burns with its characteristic *blue flame*.

Solid oxalic acid, heated upon platinum foil, evolves *white irritating vapors*. When heated in a tube open at both ends,¹ and held somewhat obliquely over a flame (to produce a gentle current of air), part of the hydrated acid is volatilized without decomposition, and recondenses upon the cool portion of the tube in *long needles*.

CHLORIDE OF BARIUM; in neutral and alkaline solutions, a white precipitate of *Oxalate of Baryta* ($\text{BaO}\bar{\text{O}}$), soluble in *hydrochloric acid*, and reprecipitated by *ammonia*.

CHLORIDE OF CALCIUM; a white precipitate of *Oxalate of Lime* ($\text{CaO}\bar{\text{O}}$), insoluble in *acetic acid*; readily soluble in *hydrochloric acid*.

NITRATE OF SILVER; a white precipitate of *Oxalate of Silver* ($\text{AgO}\bar{\text{O}}$), soluble in *nitric acid* and in *ammonia*.

ACETATE OF LEAD; a white precipitate of *Oxalate of Lead* ($\text{PbO}\bar{\text{O}}$), insoluble in *acetic acid*.

§ 343. SECOND GROUP.

Acids which are precipitated by nitrate of silver from solutions slightly acidified with nitric acid.

HYDROCHLORIC ACID (HCl)	HYDROBROMIC ACID (HBr)
HYDRIODIC ACID (HI)	HYDROSULPHURIC ACID (HS)
HYDROCYANIC ACID (HCy)	HYDROSULPHOCYANIC ACID (HCsy)
HYDROFERROCYANIC ACID (H_3Cfy)	HYDROFERRICYANIC ACID (H_3Cfdy).

HYDROCHLORIC ACID.

Solution best fitted for the reactions: Chloride of Sodium, NaCl.

NITRATE OF SILVER; in neutral and acid solutions, a white curdy precipitate

¹ Such tubes are often used in similar experiments; they should be thin, and have a diameter of from half an inch to one inch.

of *Chloride of Silver* (AgCl), which becomes violet when exposed to light; insoluble in *nitric acid*; soluble in *ammonia*, and reprecipitated by *nitric acid* in excess. If the chloride of silver be washed by decantation, dried in a porcelain capsule, and heated to redness, it fuses into oily-looking globules, which solidify into horny masses on cooling.

SULPHURIC ACID and BINOXIDE OF MANGANESE, with the aid of heat, decompose the chlorides, evolving *Chlorine*, which may be recognized by its odor, and by its property of *bleaching moist-colored papers*.

Solid chlorides (chloride of sodium) treated with CONCENTRATED SULPHURIC ACID, even in the cold, evolve *Hydrochloric Acid* (with effervescence), which may be known by its odor, and by the *thick white fumes* which it produces when escaping into the air.

Solid chlorides (in a perfectly dry state), when mixed with an excess of *bichromate of potassa*, and heated with *concentrated sulphuric acid*, in a well-dried test-tube, evolve brownish-red vapors of *Chlorochromic Acid* (see p. 334); these should be conducted, through a dry bent tube, into another (dry) test-tube surrounded with cold water; the vapors then condense into a *dark red liquid*, which is decomposed by water; if this liquid be treated with an excess of *ammonia*, it yields a yellow solution containing *Chloride of Ammonium* and *Chromate of Ammonia*, and if this be mixed with excess of *acetic acid*, and *acetate of lead*, a yellow precipitate of *Chromate of Lead* is obtained.

HYDROBROMIC ACID.

Solution best fitted for the reactions: Bromide of Potassium, KBr .

NITRATE OF SILVER; in neutral and acid solutions, a yellowish-white precipitate of *Bromide of Silver* (AgBr), which becomes violet when exposed to light; insoluble in *nitric acid*; soluble, though less easily than the chloride, in *ammonia*, and reprecipitated by *nitric acid*; if the bromide of silver be washed by decantation, dried, and heated to redness, it fuses like the chloride.

Solid bromides (bromide of potassium), treated with CONCENTRATED SULPHURIC ACID in the cold, evolve fumes of *Hydrobromic Acid* (similar to hydrochloric acid), and upon heating (especially if *binocide of manganese* be added), vapors of *Bromine*:—



the bromine-vapors may be recognized by their *red-brown color*, their peculiarly *pungent odor*, and by their action upon a little *starch-paste* (introduced on the end of a glass rod), to which they impart a fine *orange color*.

Solid bromides, when distilled with BICHROMATE OF POTASSA and CONCENTRATED SULPHURIC ACID, yield pure *Bromine*, which becomes colorless, or nearly so, when treated with excess of *ammonia*.¹

CHLORINE-WATER, added to a solution of a bromide, liberates the bromine, which imparts an *orange color* to the liquid; an excess of chlorine should be avoided, since it converts the bromine into the colorless chloride of bromine. If the solution containing the bromine be agitated with about $\frac{1}{4}$ its volume of *ether*, the latter dissolves the bromine, and, on standing, rises with it to the surface, forming a red layer above the (now nearly colorless) liquid. The ethereal solution of bromine should now be carefully decanted and agitated with solution of *potassa*, when it becomes nearly colorless, the bromine being converted into *Bromide of Potassium* and *Bromate of Potassa*; the solution is evaporated in a porcelain dish (the glaze of which will suffer), and the residue heated to redness, when the *bromate of potassa*, losing its oxygen, is converted into *bromide of*

¹ This affords a method of distinguishing it from chlorochromic acid, which, externally, it much resembles.

potassium. If this residue be now heated with *sulphuric acid* and *binocide of manganese*, *bromine vapors* are evolved, and may be recognized by the starch-test.

HYDRIODIC ACID.

Solution best fitted for the reactions: Iodide of Potassium, KI.

NITRATE OF SILVER; yellow precipitate of *Iodide of Silver* (AgI), which becomes dark when exposed to light; insoluble in *nitric acid* and in *ammonia*.

SULPHATE OF SUBOXIDE OF COPPER (a mixture of solutions of *sulphate of copper* (1 part of the crystals) and *sulphate of iron* ($2\frac{1}{2}$ parts of the crystals)); in neutral and slightly alkaline solutions; a brownish-white precipitate of *Sub-iodide of Copper* (Cu_2I).

BICHLORIDE OF PLATINUM; a *dark red color*. This reaction is mentioned, not as a test for iodine, but because it interferes with the detection of potassium, since the yellow precipitate of the double chloride of platinum and potassium cannot be distinctly seen in the dark red liquid; to obviate this difficulty, the iodine should be expelled by evaporating to dryness with *concentrated nitric acid*, and the residue may then be dissolved in water, and tested with hydrochloric acid and bichloride of platinum.

STARCH produces, with free iodine, a fine *blue* compound; since a very small quantity of iodine suffices for this purpose, starch is employed as a very delicate test for that substance. The solution to be tested should be mixed with a small quantity of starch-paste (prepared by heating starch with water till the granules have burst), and *concentrated nitric acid* (containing one of the red oxides of nitrogen [NO_2 or NO_3]) added drop by drop. An excess of nitric acid destroys the blue compound; *alkalies* have the same effect; the blue color disappears if the solution be heated. When the starch is in large excess, a *pink* or *violet* compound is formed.

Solid iodides, heated with CONCENTRATED SULPHURIC ACID, evolve *violet vapors of Iodine* which condense upon the cool part of the tube in the form of black scales; if a little *starch-paste* be exposed, on a glass rod, to these vapors, it assumes a dark brownish-purple color, which passes into the ordinary indigo-blue color of iodized starch when stirred up with water, especially if a little more starch be added.

CONCENTRATED NITRIC ACID produces a black precipitate of *Iodine* in solutions of the iodides.

HYDROSULPHURIC ACID.

Solution best fitted for the reactions: Sulphide of Ammonium, NH_4S .

NITRATE OF SILVER; black precipitate of *Sulphide of Silver* (AgS); insoluble in cold *dilute nitric acid*; soluble in *hot nitric acid*, with separation of sulphur; insoluble in *ammonia*.

ACETATE OF LEAD; black precipitate of *Sulphide of Lead* (PbS).

Sulphides, treated with SULPHURIC or HYDROCHLORIC ACID, evolve *Hydrosulphuric Acid* (with effervescence), which may be recognized by its *odor*, and by the *black tinge* which it imparts to paper impregnated with a *lead salt*.¹

Solid sulphides (sulphide of iron), when heated with NITRIC ACID, generally dissolve, with separation of sulphur, unless the acid is very concentrated.

Solid sulphides, heated in a tube open at both ends, evolve sulphurous acid, which may be recognized by its odor.

¹ Some sulphides, as those of copper and lead, do not evolve hydrosulphuric acid; another test for the presence of sulphur must be employed in such cases.

Sulphides, fused on platinum wire with *carbonate of soda*, in the *reducing flame*, exhibit the same deportment as the sulphates (see p. 532).¹

HYDROCYANIC ACID.

Solution best fitted for the reactions: Cyanide of Potassium,
 $\text{KCy}=\text{KC}_2\text{N}$.

NITRATE OF SILVER; a white precipitate of *Cyanide of Silver* (AgCy), which is not darkened by exposure to light; sparingly soluble in cold *dilute nitric acid*; soluble in the *concentrated acid*, especially on heating; readily soluble in *ammonia*, and partly reprecipitated by the careful addition of excess of nitric acid; readily soluble also in solution of *cyanide of potassium*.

When cyanide of silver is dried and heated to redness, it evolves *Cyanogen*; if the experiment be performed in a small glass tube closed at one end, the cyanogen may be recognized by its *odor*, and by its burning with a beautiful *peach-colored flame*, a residue of silver and paracyanide of silver (isomeric with the cyanide) is left.

If the cyanide of silver be heated in a crucible, only *Metallic Silver* remains, which is entirely dissolved by *nitric acid*.

A MIXTURE OF PROTOSULPHATE AND SESQUICHLORIDE OF IRON; a blue precipitate of *Sesquiferrocyanide of Iron* (Fe_3Cy_3 —*Prussian blue*);² insoluble in *dilute acids*, decomposed by *alkalies*. This is one of the most delicate and characteristic tests for hydrocyanic acid; since, however, the reaction does not take place with the free acid, the addition of an excess of alkali (*potassa*) should always precede that of the iron-salts; but as the Prussian blue would be decomposed by the alkali, it is necessary to add finally an excess of *dilute hydrochloric acid*. When the quantity of hydrocyanic acid is very minute, a bluish color is produced at first, and particles of Prussian blue are deposited after a time.

When *free hydrocyanic acid* is mixed with (*yellow*) *sulphide of ammonium* containing an excess of sulphur, *Sulphocyanide of Ammonium* is produced:—



if the solution be evaporated until the excess of sulphide of ammonium is expelled (which is known by the odor), and be then tested with *sesquichloride of iron*, the *blood-red* color of *Sesquisulphocyanide of Iron* is produced, which disappears entirely on adding solution of *chloride of mercury*.

Since mere traces of sulphocyanogen give the blood-red color, this becomes an exceedingly delicate test for hydrocyanic acid.

Dilute sulphuric and *hydrochloric acids* decompose the cyanides with evolution of *Hydrocyanic Acid*, which may be recognized by its odor. This forms the basis of an excellent process for examining for hydrocyanic acid.

The substance to be tested is placed in a rather tall vessel (a narrow beaker), and an excess of *dilute sulphuric acid* mixed with it; the mouth of the vessel is then covered with a watch-glass (concave surface downwards) moistened internally with a solution of *nitrate of silver*; the vessel is placed in a warm situation, when the vapor of *hydrocyanic acid* which is evolved produces a white film of *Cyanide of Silver*; this watch-glass may now be replaced by another, moistened with *yellow sulphide of ammonium*, and, after a short time, this may be removed, the excess of sulphide of ammonium expelled by a gentle heat, and the residue tested with *sesquichloride of iron*; lastly, the vessel may be covered with a third watch-glass, moistened with solution of *potassa*, which, after a few minutes, may be tested with the *mixed iron salts* and *hydrochloric acid*.

¹ Insoluble sulphides, fused with hydrated alkalies, yield soluble alkaline sulphides.

² $3\text{KC}_2\text{N} + \text{FeO} \cdot \text{SO}_3 = \text{K}_3\text{C}_3\text{N}_3\text{Fe} (= \text{K}_3\text{C}_3\text{N}_3\text{Fe}) + \text{K}_2\text{O} \cdot \text{SO}_3$, and
 $2\text{Fe}_2\text{Cl}_6 + 3\text{K}_2\text{C}_3\text{N}_3 = \text{Fe}_4\text{C}_3\text{N}_3 + 6\text{KCl}$

Solid cyanides, heated with *concentrated sulphuric acid*, evolve *Carbonic Oxide*, which burns with a *blue flame* :—



HYDROSULPHOCYANIC ACID.

Solution best fitted for the reactions : Sulphocyanide of Potassium,
 $\text{KC}_3\text{S} = \text{KC}_3\text{S}_3.$

NITRATE OF SILVER ; white precipitate of *Sulphocyanide of Silver* (AgC_3S) ; insoluble in *dilute nitric acid*, and in *ammonia* ; when heated to redness, sulphocyanide of silver is decomposed, leaving only *metallic silver*.

SESQUICHLORIDE OF IRON ; the dark *blood-red color*, already noticed ; destroyed by *chloride of mercury*.

HYDROFERROCYANIC ACID.

Solution best fitted for the reactions : Ferrocyanide of Potassium,
 $\text{K}_4\text{C}_6\text{F} = \text{K}_4\text{C}_6\text{F}_6.$

NITRATE OF SILVER ; a white (or nearly white) precipitate of *Ferrocyanide of Silver* ($\text{Ag}_2\text{C}_6\text{F}$) not dissolved by *dilute nitric acid* or *ammonia* ; decomposed by *heat*, the silver being reduced to the metallic state.

The reactions of this acid with the salts of iron have been given at p. 516.

HYDROFERRICYANIC ACID.

Solution best fitted for the reactions : Ferricyanide of Potassium,
 $\text{K}_3\text{C}_6\text{F}_3 = \text{K}_3\text{C}_6\text{F}_3.$

NITRATE OF SILVER ; a red-brown precipitate of *Ferricyanide of Silver* ($\text{Ag}_2\text{C}_6\text{F}_3$) ; insoluble in *dilute nitric acid* ; soluble in *ammonia* ; decomposed by *heat*, with reduction of silver.

The reactions of this acid with iron-salts have been given at p. 515.

Sulphocyanides, ferrocyanides, and ferricyanides may all evolve *Carbonic Oxide* when heated with *concentrated sulphuric acid*.

The two latter, when heated in the moist state, blacken, and evolve *Ammonia* and *Hydrocyanic Acid*.

All three salts may evolve hydrocyanic acid when heated with *hydrochloric acid*.

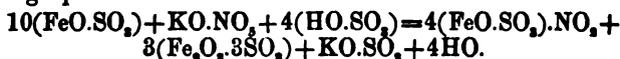
§ 344. THIRD GROUP.

Acids which are not precipitable.

NITRIC ACID (NO_3) CHLORIC ACID (ClO_3)
 HYPOCHLOROUS ACID (ClO).

NITRIC ACID.

If a solution of a nitrate (nitrate of potassa) be mixed with about half its volume of *concentrated sulphuric acid*, the mixture allowed nearly to cool, and a crystal of *sulphate of iron* then dropped into it, a *brown ring* will be found around the crystal ; this ring will only appear when the solution has been allowed to stand for some time ; *agitation and elevation of temperature should be avoided*, since they tend to decompose the brown *Compound of Binoxide of Nitrogen with Sulphate of Iron* ; the formation of this compound is explained by the following equation :—



If the above-mentioned precautions be attended to, we may detect very small quantities of nitric acid by this test.

If a solution of a nitrate (nitrate of potassa) be colored distinctly blue with solution of indigo (sulphindigotic acid), and be then heated with a little concentrated sulphuric acid, the blue color will give place to a yellow.

Solid nitrates (nitrate of potassa) when heated with CONCENTRATED SULPHURIC ACID, evolve fumes of Nitric Acid, often accompanied by red-brown vapors of Peroxide of Nitrogen.

If a solid nitrate be heated with concentrated sulphuric acid and metallic copper, red-brown fumes of Peroxide of Nitrogen are evolved.

Solid nitrates, heated with hydrochloric acid (concentrated) evolve Peroxide of Nitrogen and Chlorine.

If a nitrate be heated on charcoal before the blowpipe, the charcoal burns with deflagration, at the expense of the oxygen furnished by the salt.

When cyanide of potassium in small quantity is fused with nitre upon platinum foil, pretty violent deflagration ensues, consequent upon the sudden evolution of carbonic acid and nitrogen, caused by the oxidation of the cyanogen.

CHLORIC ACID.

A solution of a chlorate (chlorate of potassa) behaves, with indigo and sulphuric acid, like a nitrate.

If a small quantity of a solid chlorate (chlorate of potassa) be dropped into CONCENTRATED SULPHURIC ACID, the solution immediately assumes a deep yellow color, and if it be heated, an explosion often ensues, from the sudden evolution and decomposition of the Peroxide of Chlorine (ClO_2). In the cold, the latter is slowly evolved, and may be recognized by its deep yellow color and peculiar odor.

Solid chlorates, when heated with concentrated hydrochloric acid, evolve *Es-chlorine* (see p. 188), which may be known by its deep yellow color, by its peculiar odor, and by its exploding feebly by contact with flame.

Chlorates, like nitrates, deflagrate, but much more vividly, on charcoal, and with cyanide of potassium.

HYPOCHLOROUS ACID.

Solution best fitted for the reactions: An aqueous solution of bleaching-powder ($\text{CaO} \cdot \text{ClO} + \text{CaCl}$).

Solutions of the hypochlorites bleach organic coloring matters (indigo, litmus, &c.) very readily, especially when mixed with a little free acid.

SULPHATE OF MANGANESE gives, with solutions of hypochlorites, a black precipitate of Binoxide of Manganese.

Hypochlorites evolve chlorine when heated with sulphuric and hydrochloric acids.

ORGANIC ACIDS.

§ 845. The first group of organic acids comprehends those which are immediately blackened when heated with concentrated sulphuric acid—viz. tartaric, tannic, and gallic acids.

In the second group we find citric and uric acids, which are not volatile without decomposition, but are not immediately blackened when heated with concentrated sulphuric acid.

The third group includes those acids which are volatile without decomposition; benzoic, succinic, and acetic acids.

§ 346. FIRST GROUP.

Acids which are immediately blackened when heated with concentrated sulphuric acid.

TARTARIC ACID ($C_4H_4O_6 = \overline{T}$)

TANNIC ACID ($C_{22}H_2O_9 = \overline{Qt}$)

GALLIC ACID ($C_7H_6O_5 = \overline{G}$)

TARTARIC ACID.

Solution best fitted for the reactions: Tartrate of Soda, $2NaO.\overline{T}$.

(A perfectly neutral solution of this salt is best prepared, extemporaneously, as follows: an aqueous solution of tartaric acid is mixed with solution of carbonate of soda, until, after heating the liquid to expel the free carbonic acid, it has only a slightly acid reaction; a small excess of ammonia is then added, and the solution gently evaporated until perfectly neutral.)

CONCENTRATED SULPHURIC ACID, heated with (solid) tartaric acid, or a tartrate decomposes it with separation of *Carbon*, which renders the mixture *black*; *Carbonic Oxide* (burning with a *blue flame*) is evolved at the same time.

Solid tartaric acid or a tartrate, when heated on platinum foil, chars, often inflames, burning with a pale flame, and evolves a peculiar *odor of burnt sugar*, which is perceived more readily when the substance is heated in a tube open at both ends.

CHLORIDE OF CALCIUM; in neutral or slightly alkaline solutions, a white precipitate of *Tartrate of Lime* ($2CaO.\overline{T}$); somewhat soluble in water, soluble in solution of *chloride of ammonium*;¹ soluble also in *potassa*, and reprecipitated on boiling; soluble in *acetic acid*. The presence of ammoniacal salts always retards or prevents this precipitation, which is, on the contrary, promoted by the addition of free *ammonia*.

CHLORIDE OF BARIUM; in neutral or slightly alkaline solutions, a white precipitate of *Tartrate of Baryta* ($2BaO.\overline{T}$); soluble in *ammoniacal salts*; soluble in *hydrochloric acid*.

NITRATE OF SILVER; a white precipitate of *Tartrate of Silver* ($2AgO.\overline{T}$); readily soluble in *acids* and in *ammonia*.

TANNIC ACID.

Solution best fitted for the reactions: Aqueous solution of tannic acid, \overline{Qt} .

CONCENTRATED SULPHURIC ACID, heated with (solid) tannic acid produces, immediately, a dark, purplish-black liquid, but does not evolve carbonic oxide.

When heated on platinum, tannic acid burns, chars, and emits a peculiar odor.

ALKALIES, added to a solution of tannic acid, cause it to absorb oxygen from the air, and to assume a *brown color*.

SESQUICHLORIDE OF IRON; a bluish-black precipitate of *Tannate of Sesquioxide of Iron* ($Fe_2O_3.\overline{Qt}$).

DILUTE SULPHURIC (OR HYDROCHLORIC) ACID produces, in a pretty concentrated solution of tannic acid, a *white precipitate*, which is an insoluble compound of the two acids.

¹ When this precipitate is highly crystalline, it is most difficult to redissolve it in chloride of ammonium.

GALLIC ACID.

Solution best fitted for the reactions: Aqueous solution of gallic acid, \bar{G} .

CONCENTRATED SULPHURIC ACID behaves, with gallic acid, much in the same way as with tannic acid.

Heat also affects it in a similar manner, though the odor is different.

ALKALIES cause the solution of gallic acid to *change color* very rapidly.

SESQUICHLORIDE OF IRON; a *bluish-black* precipitate.

§ 347. SECOND GROUP.

Acids which are not immediately blackened when heated with concentrated sulphuric acid.

CITRIC ACID ($C_6H_8O_7 = \bar{C}_i$).

URIC ACID ($C_5H_4N_4O_6 = \bar{U}$).

CITRIC ACID.

Solution best fitted for the reactions: Citrate of Soda, $3NaO.\bar{C}_i$.

(This solution may be prepared exactly as recommended in the case of tartaric acid.)

CONCENTRATED SULPHURIC ACID, when heated with citric acid, decomposes it with evolution of *Carbonic Oxide*, which burns with a *blue flame*; the mixture blackens only after long boiling.

Citric acid, when heated on platinum foil, chars, and burns with a *pale flame*; when heated in a tube open at both ends, it evolves *irritating vapors*.

CHLORIDE OF CALCIUM, added to a neutral solution of a citrate, does not immediately produce a precipitate unless the solution be very concentrated, but, on boiling, *Citrate of Lime* ($3CaO.\bar{C}_i$) being less soluble in hot water than in cold, is immediately precipitated; it is soluble in much water; insoluble in *potassa*; soluble (though with some difficulty) in *chloride of ammonium*; the presence of free *ammonia* promotes the precipitation, while *ammoniacal salts* prevent it.

CHLORIDE OF BARIUM; a white precipitate of *Citrate of Baryta* ($3BaO.\bar{C}_i$); soluble in much water, in free *acids* and in *ammoniacal salts*.

NITRATE OF SILVER; a white precipitate of *Citrate of Silver* ($3AgO.\bar{C}_i$), readily soluble in *nitric acid* and in *ammonia*.

URIC ACID.

CONCENTRATED SULPHURIC ACID, with the aid of heat, dissolves uric acid without change; if the heat be long continued, the liquid becomes dark.

Uric acid, when heated alone, evolves an odor of *Ammonia* and *Hydrocyanic Acid*, followed by an odor similar to that of *burnt hair*; it leaves a dark carbonaceous residue.

Uric acid is almost insoluble in water and in hydrochloric acid.

DILUTE NITRIC ACID, with the aid of heat, dissolves uric acid with effervescence and evolution of red fumes, the uric acid being oxidized at the expense of the nitric acid. If the nitric solution be evaporated just to dryness, it leaves a *yellow* residue, which becomes *reddish* on further heating, and assumes a fine *purple-red color* on the gradual addition of *ammonia* in excess; this reaction is due to the production of a peculiar purple body, termed *Murexide*, resulting from the action of ammonia upon the products of oxidation of uric acid.

In applying this test to very small quantities of material, a piece of platinum foil, or a small capsule of that metal may be employed.

POTASSA (*diluted*) readily dissolves uric acid, which is reprecipitated from the solution as a white crystalline powder on adding *hydrochloric acid*.

§ 348. THIRD GROUP.

Acids which are volatile without decomposition.

BENZOIC ACID ($C_{14}H_8O_2 = \overline{Bz}$)

SUCCINIC ACID ($C_6H_8O_4 = \overline{S}$)

ACETIC ACID ($C_2H_4O_2 = \overline{A}$).

BENZOIC ACID.

Solution best fitted for the reactions: Benzoate of Oxide of Ammonium
 $NH_4O.\overline{Bz}$.

(Prepared by dissolving benzoic acid in solution of ammonia, and evaporating at a gentle heat, until the solution is no longer alkaline.)

Benzoic acid, heated on platinum foil, volatilizes, in great part, without decomposition, yielding highly irritating vapors, having the odor of frankincense; if the flame be allowed to play upon it, it burns with a bright, smoky flame. When heated in a tube open at both ends, a portion of the acid condenses in feathery crystals, upon the cool part of the tube.

When heated with CONCENTRATED SULPHURIC ACID, benzoic acid volatilizes, with its peculiar odor, but is not blackened.

NITRATE OF SILVER, in neutral solutions, a white precipitate of *Benzoate of Silver* ($AgO.\overline{Bz}$) readily soluble in *nitric acid* (with separation of benzoic acid, if the solution be concentrated) and in *ammonia*.

SESQUICHLORIDE OF IRON; in neutral solutions, a pale buff precipitate of *Benzoate of Sesquioxide of Iron* ($Fe_2O_3.3\overline{Bz}$); *ammonia* in excess withdraws the benzoic acid from this precipitate, leaving only the hydrated sesquioxide of iron.

HYDROCHLORIC ACID precipitates benzoic acid from its solutions, if they be not too dilute, in white crystalline flakes.

SUCCINIC ACID.

Solution best fitted for the reactions: Succinate of Oxide of Ammonium,
 $3NH_4O.\overline{S}$.

(Prepared in the same way as the benzoate.)

Succinic acid, heated on platinum foil, evolves vapors which excite an involuntary fit of coughing; when inflamed, it burns with a much paler flame than benzoic acid; if heated in a tube open at both ends, a great part of it sublimes.

It behaves, with CONCENTRATED SULPHURIC ACID, like benzoic acid.

NITRATE OF SILVER; same result with succinic acid as with benzoic.

SESQUICHLORIDE OF IRON, in neutral solutions, a red-brown precipitate (*Succinate of Sesquioxide of Iron*) which is decomposed by *ammonia*.

CHLORIDE OF BARIUM does not precipitate a solution of a succinate, even after addition of free *ammonia*, but if *alcohol* be added a white precipitate is produced.

ACETIC ACID.

Heat decomposes the solid acetates (acetate of potassa, *e. g.*), with evolution of vapor of *Acetone* (C_3H_6O) which has a peculiar *aromatic odor*, and burns with a pale flame.

Acetates, when heated with CONCENTRATED SULPHURIC ACID, evolve *Acetic Acid*, known by its odor of vinegar.

When heated with *concentrated sulphuric acid* and *alcohol*, the acetates furnish *Acetic Ether* ($C_2H_5O.C_2H_3O_2$) which is characterized by a most agreeable *aromatic odor*, more readily perceived when the solution cools.

SESQUIOCHLORIDE OF IRON produces, in neutral solutions of acetates (acetate of potassa), the fine *red color* of *Acetate of Sesquioxide of Iron* ($Fe_2O_3.A$) which does not disappear on addition of *chloride of mercury*.

NITRATE OF SILVER; in neutral, pretty concentrated solutions, a white crystalline precipitate of *Acetate of Silver* ($AgO.A$) readily soluble in *nitric acid*, and in *ammonia*.

SYSTEMATIC COURSE FOR THE ANALYSIS OF SUBSTANCES WHICH MAY CONTAIN ALL THE MORE FREQUENTLY OCCURRING BASES AND ACIDS.

§ 349. In the following systematic course, we proceed upon the supposition that the substance under examination is solid, and is neither a metal nor an alloy, since, in the analysis of substances of this description, special methods are followed, which will be described hereafter.

The process of analysis is divided into the five following parts:—

1. The *mechanical division of the substance* which is necessary to facilitate the action of solvents.
2. The *preliminary examination*, consisting of a few simple experiments, from which we may obtain very valuable information as to the nature of the substance, before proceeding to the regular analysis.
3. The *process of solution*, in which the substance is treated with water and acids; or, if it be insoluble in these, is fused with alkaline carbonates, in order to reduce it to a fit state for the application of reagents.
4. The *treatment with general reagents* which serve to indicate the groups to which the bases and acids present belong.
5. The *special examination* for the individual members of each group.

The processes for the detection of bases and of acids, though separately conducted, are founded upon the same broad principles.¹

MECHANICAL DIVISION OF THE SUBSTANCE.

§ 350. The substance intended for analysis should first be coarsely pounded in an iron or Wedgwood mortar (according to its hardness), and afterwards ground to powder. Few substances require any further preparation, but in some cases, small hard fragments remain intermixed with the powder; these should be separated from the latter, by rubbing, with a pestle, or with the fingers, upon a piece of muslin stretched across the mouth of a beaker; any fragments remain-

¹ We may remind the student, that all the *manipulated* analytical operations have been fully described in a §

ing upon the muslin must be powdered and sifted until entirely reduced. The whole of the powder should be well mixed before separating any portion for analysis.

EXAMINATION FOR BASES.

§ 351. PRELIMINARY EXAMINATION.

Experiment 1.—A small portion of the powder¹ is heated in a glass tube open at both ends, and held somewhat obliquely, to allow of the passage of a slow current of air.²

I. The substance *volatilizes*, either entirely or partly:—presence of compounds of *ammonium, mercury, arsenic, antimony, or cadmium, or of sulphur, oxalic acid, or some organic substance.*

Fumes are evolved, having the *odor of burning sulphur*:—presence of SULPHUR or of a SULPHIDE.

The fumes have the *odor of garlic*:—presence of ARSENIC.

A white *amorphous sublimate* is formed upon the cool part of the tube:—presence of a compound of AMMONIUM, CADMIUM, or MERCURY. (The sublimate of *arsenic acid* sometimes appears amorphous to the unassisted eye.)

A white *sublimate of minute (octohedral) crystals* is formed upon the side of the tube:—probably ARSENIOUS ACID.

A *sublimate composed of very distinct crystals* is formed:—probable presence of certain ORGANIC ACIDS (see p. 545).

A *gray sublimate* is formed:—probably consists of globules of MERCURY, which unite into larger globules when rubbed with a glass rod.

The *sublimate is yellow*:—probably SULPHUR.

II. The substance *changes color*, without evolution of odor:—probable presence of a *heavy metallic oxide*.³

The substance *blackens*, at the same time evolving a *peculiar odor*:—presence of *organic matter*.

III. Deflagration or detonation takes place.

Presence of a *nitrate or chlorate*, together with combustible matter.

Exp. 2. The substance is heated, on charcoal, with carbonate of soda, in the reducing flame of the blowpipe, the oxidizing flame being allowed to spread over the charcoal⁴ (see p. 109). Should no reduced metal make its appearance after exposure for two or three minutes to the flame, a little cyanide of potassium may be added, and the experiment continued.

If no metal is visible at the end of the operation, the test specimen and surrounding particles of charcoal should be levigated as directed at p. 109.

I. A *metallic globule* is obtained.

The globule is tested as to its malleability (p. 109).

Malleable:—LEAD (makes a black streak upon paper); a *yellow incrustation* is formed upon the charcoal. TIN; a slight white incrustation. COPPER (known by its color). SILVER.

Semi-malleable:—BISMUTH; a *yellow incrustation*.

¹ Even small crystals should be reduced to powder, since otherwise they are liable to decrepitate.

² This experiment is sometimes made in an iron spoon, but it is obvious that several valuable indications are then lost.

³ All oxides fall under this designation, except the alkalies, the alkaline earths, and the earths proper (alumina, glucina, &c.).

⁴ Should sulphur be present, the substance should be roasted for some time in the *open flame*, as directed at p. 109; but it must then be remembered that arsenic and cadmium may have volatilised during the roasting.

Brittle:—ANTIMONY; abundant *white incrustation*.

II. No globule is obtained, but shining *metallic spangles* are observed after levigation: probably *tin*, *antimony*, or *copper*.

III. No metal is obtained, but merely an *incrustation* on the charcoal.

The incrustation is *white*: probably due to ZINC (the incrustation is *yellow while hot*). ARSENIC; a *garlic odor* is perceived during the experiment. Salts of *ammonium* and *mercury*.

The incrustation is *brown*: presence of CADMIUM.

IV. If a *deflagration* be observed in this experiment, it indicates the presence of a *nitrate* or *chlorate*.

V. If a light-colored *infusible, highly incandescent mass* be left upon the charcoal, it is probable that either *silica*, an *alkaline earth*, or an *earth*, or *oxide of zinc*, is present.

Exp. 3.—The substance is added, by small portions at a time, to a bead of borax, and heated, first in the *outer*, then in the *inner* blowpipe-flame, the color produced in each case being carefully observed, both in the hot and cold bead (*see p. 109*).

I. A *green bead* is obtained in the outer flame: presence of CHROMIUM; the color varies from greenish-yellow to yellowish-green in the outer flame, and becomes a pure *emerald green* in the inner flame. COPPER; bluish-green (or greenish-blue), either disappearing entirely, or requiring a partial *opaque-red* color in the inner flame.

II. A *reddish-yellow* bead is obtained in the outer flame; presence of IRON; the color either vanishes or fades, on cooling, and becomes *bottle-green* in the inner flame. NICKEL; the color vanishes or fades on cooling, and becomes *dusky purple* or *gray* in the inner flame. If a minute particle of nitre be now added to the bead, and the latter again exposed to the outer flame, it acquires a *bluish-purple* tint.

III. A *violet or pink (amethyst)* bead is obtained in the outer flame: presence of MANGANESE: the color vanishes on long exposure to the inner flame.

IV. A *blue bead* is obtained in the outer flame: presence of COBALT; the color is pure blue, and unchanged by exposure to the inner flame. COPPER; greenish-blue (or bluish-green), either vanishing or becoming tinged *opaque red* in parts, in the inner flame.

Exp. 4.—A portion of the substance is mixed, in a dish, with hydrate of lime and a little water, and a gentle heat applied.

Pungent vapors are evolved, which yield *white fumes with hydrochloric acid*, and are *alkaline* to moistened test-papers. Presence of AMMONIA.

THE PROCESS OF SOLUTION.

§ 352. The following general method of dissolving a substance to be submitted to analysis, is laid down upon the supposition that the analyst is totally ignorant of the nature of the substance (which is comparatively seldom the case), and, in many instances, the same result (*vis.* the complete solution of the matter) may be arrived at by a much less circuitous path, the discovery of which, however, must obviously be left to the judgment (guided by experience) of the analyst himself.

Before describing the process of solution, it may be well to observe that when a residue is left after treatment with any solvent, it should be well washed, if possible, by decantation, since another solvent may be much more easily applied to a residue in a test-tube than to one which has been thrown upon a filter.

I. A small portion (about 20 grs.) of the substance is *boiled with a moderate quantity* (2 or 3 drachms) of water, in a test-tube; if any residue remains, it is allowed to subside in the tube, if possible, the supernatant liquid is poured off, and a drop or two of the filtrate evaporated upon platinum; if a considerable residue be obtained, the aqueous solution

II. The residue insoluble in water is washed once or twice, if possible, by decantation; this residue is boiled with concentrated hydrochloric acid (unless silver or lead be suspected, when concentrated nitric acid should be employed), water then added, the whole again boiled, the residue, if any, allowed to subside, and the supernatant liquid filtered.

III. The portion left undissolved by hydrochloric acid is washed twice or thrice with water, and boiled with concentrated nitric acid (of course, if nitric acid was employed before, hydrochloric acid must be used here); should this fail to dissolve it, a few drops of concentrated hydrochloric (or nitric) acid are added, the whole again boiled, diluted with water and the boiling repeated. If any residue remain after this treatment with nitro-hydrochloric acid, it is collected upon a filter, washed, dried, and set aside for examination by Table VIII.

If the analyst desire to ascertain in what forms of combination the various constituents of the substance exist (as is usually the case in the analysis of artificial products), he must examine the aqueous solution separately from the acid solutions. The examination is conducted according to Table I.

If a solution in nitric acid has been prepared, it must be tested with a little hydrochloric acid, and should this produce any precipitate, a sufficient quantity must be added to separate the silver or lead as completely as possible from the solution; the precipitate is set aside for examination by Table II., and the filtrate is mixed with the other acid solution of the substance (the subsequent process being conducted as in the following case).

Should hydrochloric acid have been employed first, the two acid solutions may be mixed together, and if any precipitate result from the mixture, it may be gently warmed with a slight excess of hydrochloric acid, and if not dissolved, analyzed as an insoluble substance. The mixed acid solutions should be carefully evaporated to a very small bulk, to expel the greater portion of the acid, then diluted with water strongly acidulated with hydrochloric acid, and analyzed according to Table I, omitting, of course, the addition of hydrochloric acid.

If, however, the arrangement of the constituents be a matter of indifference, the aqueous solution may be mixed with hydrochloric acid, in order to separate any silver, lead, or suboxide of mercury (Table II.), and afterwards added to the acid solutions of the substance; any precipitate which is thus produced is warmed with hydrochloric acid, and, if undissolved, analyzed as an insoluble substance (Table VIII.).

The mixed solutions are evaporated to expel excess of acid, diluted with water (strongly acidulated with hydrochloric acid), and examined by Table I, omitting to add more hydrochloric acid.

TREATMENT WITH GENERAL REAGENTS.

§ 353. In using the following general table, the analyst will at once appreciate the great economy of time which will result from his proceeding always according to some regular plan. Thus, it is advantageous to make the filtrate the chief object of attention, setting aside each precipitate, as it is obtained, for subsequent examination. These precipitates may be well washed whilst the operator is proceeding with the filtrate.

Again, the time occupied in the evaporation of the filtrate from the sulphuretted hydrogen precipitate may be employed in the examination of the latter, or of the precipitate produced by hydrochloric acid.

Such arrangements as these will readily suggest themselves to every analyst, and will be found to shorten very considerably the time occupied by the whole process, especially when he is sufficiently well versed in it to examine more than one substance at the same time.

TABLE I.—GENERAL TABLE FOR THE EXAMINATION FOR BASES.

<p>To the greater portion of the original solution add HYDROCHLORIC ACID in excess, and heat gently (Note 1).</p>	
<p><i>Precipitate may contain</i> Chloride of Silver Subchloride of Mercury Chloride of Lead <i>Examined by Table II.</i></p>	<p>The filtrate (Note 2) is largely diluted with WATER, completely saturated with SULPHURIC ACID, and gently heated (Note 3).</p> <p>The filtrate is evaporated till the odor of sulphuretted hydrogen has disappeared, mixed with a little concentrated NITRIC ACID, and evaporated to dryness on the sand-bath; if the preliminary examination has indicated the presence of oxalic acid, or of organic matter, this residue is heated to redness in air, but not otherwise (Note 4). This residue is mixed with a little concentrated HYDROCHLORIC ACID, a small quantity of WATER added, and the mixture digested on a sand-bath, until it is either completely dissolved, or only a white residue of silica remains (Note 5). To this solution are added CALCIUM HYDROXIDE, AMMONIA in excess, and SULPHURIC ACID in slight excess; the mixture is then heated to boiling (Note 6).</p>
<p><i>Precipitate may contain</i> Sulphide of Lead " Mercury " Copper " Cadmium Tersulphide of Bismuth Sulphide of Tin Bisulphide of Tin Tersulphide of Antimony Pentasulphide of Antimony Tersulphide of Arsenic " Gold Bisulphide of Platinum <i>Examined by Table III.</i></p>	<p>The filtrate (Note 6) is mixed with a little AMMONIA, solution of EMERSONIAN SALTS or AMMONIA added as long as any precipitate is formed, and a gentle heat applied for a few minutes (Note 9).</p> <p><i>Precipitate may contain</i> Carbonate of Baryta " Strontia " Lime <i>Examined by Table V.</i></p>
<p><i>Precipitate may contain</i> Alumina Phosphate of Alumina Sesquioxide of Chromium Phosphate of Baryta " Strontia " Lime " Magnesia Sulphide of Iron " Cobalt " Nickel " Manganese " Zinc (Note 7). <i>Examined by Table IV.</i></p>	<p>The filtrate is divided into two parts, the one having about three times the volume of the other.</p> <p>To the smaller part is added (first, a little CALCIUM HYDROXIDE, AMMONIA, to prove that all the baryta, strontia, and lime have been removed, and then) POTASSIUM CYANIDE or SODA; the solution is well agitated, and allowed to stand for some time; <i>White crystalline precipitate, presence of Magnesia.</i></p> <p>The remaining portion is evaporated to dryness, and ignited till no more fumes (of ammoniacal salt) are evolved. The residue is tested for soda by taking a portion upon a modelnet (thin platinum wire, and exposing it in the lower blow-pipe-flame; <i>A yellow color imparted to the outer flame indicates the presence of Soda.</i></p> <p>The remaining portion is dissolved in a little water, the solution acidulated with HYDROCHLORIC ACID, and the crystals of BARIUM CHLORIDE or POTASSIUM CHLORIDE added; the solution is agitated, and allowed to stand for some time. <i>Yellow crystalline precipitate, presence of Potassa.</i> (Note 10.)</p>

*. Ammonia will have been sought in the preliminary examination.

TABLE II.—ANALYSIS OF THE PRECIPITATE PRODUCED BY HYDROCHLORIC ACID. (Note 1.)

The precipitate is washed once or twice with a little cold WATER (by decantation, if possible, the washings being added to the filtrate), and boiled with a considerable amount of WATER (Note 2); the clear solution is decanted from the residue.

<p><i>Residue may contain</i> Chloride of Silver Subchloride of Mercury</p> <p>Washed by decantation, and heated gently with excess of AMMONIA.</p>	<p><i>Solution may contain</i> Chloride of Lead Add DILUTE SULPHURIC ACID. <i>White Precipitate,</i> Sulphate of Lead Presence of Lead.</p>
<p><i>Residue</i> (Black) Suboxide of Mercury.</p>	<p><i>Solution may contain</i> Chloride of Silver Add excess of DILUTE NITRIC ACID. <i>Precipitate</i> becomes violet when exposed to light, dissolves easily in AMMONIA. Presence of Silver.</p>

TABLE III.—ANALYSIS OF THE PRECIPITATE PRODUCED BY HYDROSULPHURIC ACID.

Gold and Platinum must be specially tested for, according to the methods described at pp. 151 and 152, in separate portions of the original solution, after addition of Hydrochloric Acid.

The precipitate is well washed upon the filter, transferred to a test-tube, or small flask, and boiled with Yellow Sulphide of Arsenium for some minutes (Note 1). By this treatment, the precipitate is divided into two portions, which must be examined separately.

EXAMINATION OF THE PORTION SOLUBLE IN SULPHIDE OF AMMONIUM.

The Sulphide of Arsenium solution may contain

Pentarsulphide of Antimony, Bisulphide of Tin, Pentarsulphide of Arsenic
(with traces of Sulphide of Copper, Bisulphide of Platinum, Tersulphide of Gold, and Sulphide of Mercury).

It is mixed with excess of DILUTE HYDROCHLORIC ACID, and a little strong solution of HYDROCHLORIC ACID.

The above sulphides are reprecipitated, and must be washed, and settled with solution of SESQUICARBONATE OF AMMONIA, which should remain in contact with the precipitate for about fifteen minutes (a gentle heat being applied if much Arsenic be present).

Residue may contain

Bisulphide of Tin, Pentarsulphide of Antimony

(with traces of Sulphide of Copper, Bisulphide of Platinum, Tersulphide of Gold, and Sulphide of Mercury). Washed with a solution of SESQUICARBONATE OF AMMONIA, till the washings no longer give a notable yellow precipitate with HYDROCHLORIC ACID, and dissolved off the filter in as little hot NITRO-HYDROCHLORIC ACID as possible.

The solution is mixed (in a beaker, or large test-tube) with excess of SESQUICARBONATE OF AMMONIA, and boiled for a minute or two (a blue color indicates copper).

Precipitate may contain

Binoxide of Tin.

Washed with a little SESQUICARBONATE OF AMMONIA, dried, and treated as directed in Note 1.

Solution may contain

Antimonious Acid.

(with traces of Oxide of Copper, Tersulphide of Gold, Binoxide of Platinum, and Oxide of Mercury).

Mixed with a slight excess of HYDROCHLORIC ACID, and saturated with HYDROSULPHURIC ACID.

If the precipitate be orange

(Pentarsulphide of Antimony);

it indicates the presence of

Antimony,

and no further steps are necessary; but if it be not orange, it must be collected on a filter, washed, boiled with CONCENTRATED AMMONIA, a few bubbles of HYDROSULPHURIC ACID passed, and the solution filtered.

Residue may contain

(traces of Sulphide of Copper, Tersulphide of Gold, Bisulphide of Platinum, and Sulphide of Mercury).

Solution may contain

Pentarsulphide of Antimony.

Mixed with excess of HYDROCHLORIC and HYDROSULPHURIC ACIDS.

Orange precipitate,

Presence of

Antimony.

Solution may contain

Pentarsulphide of Arsenic,

Bisulphide of Tin

(N^o. 1, 8). (with traces of Pentarsulphide of Antimony Sulphide of Copper). Washed with excess of DILUTE HYDROCHLORIC ACID, and the resulting precipitate divided into two parts, which should be collected upon separate filters.

Part 1.

Washed, dissolved off the filter in warm AMMONIA, the solution evaporated to dryness on a water bath, and the residual

Pentarsulphide of Arsenic

tested by the method of Freudenthal (No. 1249).

Part 2.

Washed till free from COLORS (test with NITRATE OF SILVER), dried, and de-fragrated (paper and all, if necessary, Note 9) with NITRATE of Potassa; the fused mass boiled with WATER, the solution acidulated with NITRIC ACID and boiled.

White precipitate,

Probably

Binoxide of Tin;

collected on a filter, and treated as directed in Note 7.

TABLE III.—EXAMINATION FOR BASES.

TABLE III. (continued).—EXAMINATION OF THAT PORTION OF THE PRECIPITATE PRODUCED BY HYDROSULPHURIC ACID WHICH IS INSOLUBLE IN SULPHIDE OF AMMONIA.

<i>Residues may contain</i>	
<p>Sulphide of Mercury, Sulphide of Lead, Terralpbide of Copper, Sulphide of Cadmium, Bisulphide of Tin (Note 2)</p> <p>(Terralpbide of Gold, Bisulphide of Platinum, with traces of the Pentarsulphides of Antimony and Arsenic).</p> <p>Washed till the washings are not precipitated by NITRAC ACID (Note 3), and boiled with DILUTE NITRAC ACID.</p>	<p style="text-align: center;"><i>Residues may contain</i></p> <p>Oxide of Lead, Peroxide of Bismuth, Oxide of Copper, Oxide of Cadmium (Binoxide of Platinum, with traces of Oxide of Mercury, and Peroxide of Gold).</p> <p>Evaporated, if necessary, to a small bulk, to expel excess of NITRAC ACID, mixed with DILUTE SULPHURIC ACID, and allowed to stand for some time (ten minutes).</p>
<p style="text-align: center;"><i>Residues may contain</i></p> <p>Sulphide of Mercury, Sulphide of Cadmium (Note 4), Binoxide of Tin (Note 2)</p> <p>(Antimonie Acid, traces, Sulphate of Lead, traces, Bisulphide of Platinum, Gold).</p> <p>A part of this residue is tested for</p> <p style="text-align: center;">Mercury</p> <p>by dissolving in NITRO-HYDROCHLORIC ACID, adding excess of AMMONIA, then a slight excess of HYDROCHLORIC ACID, and boiling with slips of COPPER WIRE, which are afterwards washed, and heated in a tube (see p. 619).</p> <p style="text-align: center;">Cadmium (Note 4)</p> <p>may be detected in the remainder of the residue by incinerating the filter, and fusing the ash with CITRAC or POTASSUM, in a closed crucible; if a red-brown sublimate be formed upon the lid of the crucible, it should be dissolved in HYDROCHLORIC ACID, and tested with HYDRO-SULPHURIC ACID;</p> <p style="text-align: center;">A yellow precipitate indicates Cadmium.</p> <p style="text-align: center;">Tin</p> <p>may be detected by boiling the above fused mass with WATER, allowing the metallic particles to subside, pouring off the supernatant liquid, and boiling the metal with HYDROCHLORIC ACID; if the solution be diluted with WATER, filtered, and tested with CHLORINE or MANGANESE,</p> <p style="text-align: center;">A white or gray precipitate will indicate Tin.</p>	<p style="text-align: center;"><i>Residues may contain</i></p> <p>Peroxide of Bismuth,</p> <p>to be dissolved in DILUTE NITRAC ACID, with a little HYDROCHLORIC ACID, evaporated just to dryness, the residue re-dissolved in WATER, with 2 drop of HYDROCHLORIC ACID, and much WATER added.</p> <p>A solution mixed with a little HYDROCHLORIC ACID, and saturated with HYDRO-SULPHURIC ACID, and saturated with HYDRO-SULPHURIC ACID.</p> <p>The precipitate is well washed, till the washings have only a feeble acid reaction, and boiled with DILUTE SULPHURIC ACID (Note 6).</p> <p style="text-align: center;"><i>Residues may contain</i></p> <p>Sulphide of Copper (Bisulphide of Platinum, with traces of Sulphide of Mercury and Terralpbide of Gold).</p> <p>Dissolve in a little CONCENTRATED NITRAC ACID, add excess of AMMONIA, then excess of ACETIC ACID and FERRIC OXYGENIDE OF POTASSIUM.</p> <p>Red-brown precipitate or color, due to Ferricyanide of Copper; Presence of Copper.</p>
<p style="text-align: center;"><i>Precipitate, Sulphate of Lead.</i></p> <p style="text-align: center;">Presence of Lead.</p>	<p style="text-align: center;"><i>Solution</i></p> <p>Mixed with excess of AMMONIA.</p>

TABLE V.—ANALYSIS OF THE PRECIPITATE PRODUCED BY CARBONATE OF AMMONIA.

<p>I. Tested with SULPHATE OF LIME. <i>Precipitate formed immediately,</i> Presence of Baryta.</p> <p>— <i>Precipitate only after standing,</i> Presence of Strontia. (Note 1.)</p>	<p>II. Mixed with a saturated solution of SULPHATE OF POTASSA, and allowed to stand for some time.</p> <p><i>Precipitate,</i> Sulphate of Baryta and Sulphate of Strontia (and perhaps a little Sulphate of Lime), (Note 2.)</p> <p><i>Solution may contain</i> Sulphate of Lime, AMMONIA and OXALATE OF AMMONIA added. <i>White precipitate,</i> Oxalate of Lime. Presence of Lime.</p>	<p>III. Mixed with excess of HYDROFLUOSILICIC ACID, and evaporated to dryness; the residue extracted with ALCOHOL.</p> <p><i>Residue,</i> Silicofluoride of Barium. (Note 3.)</p> <p><i>Solution may contain</i> Chloride of Strontium, Chloride of Calcium.</p> <p>Evaporated to dryness [residue tested before the blowpipe for Strontia (p. 512)]; dissolved in WATER, the solution divided into two parts.</p> <p>The smaller portion is tested with HYDROFLUOSILICIC ACID, to ascertain that all the Baryta is separated (Note 4.)</p> <p>The other portion is mixed with SULPHATE OF LIME. <i>White precipitate after some time,</i> Presence of Strontia</p>
---	--	---

The precipitate is washed, and dissolved off the filter in as little DILUTE HYDROCHLORIC ACID as possible. The solution is divided into three parts.

NOTES TO TABLE I.

1. It must be borne in mind that certain *oxychlorides*, e. g. those of *antimony* and *bismuth*, may be precipitated upon the first addition of hydrochloric acid; these redissolve, however, in an excess of the latter, which should therefore be added as long as it appears to diminish the quantity of the precipitate.

2. If *arsenic* have been detected in the preliminary examination, this filtrate must now be completely saturated with sulphurous acid (*for the mode of preparation, see p. 157*), and evaporated to expel excess of this reagent, which reduces the *arsenic acid* to the state of *arsenious*. If *baryta, strontia, or oxide of lead* be present, the sulphurous acid will give rise to a precipitation of the sulphates of these oxides; the precipitate should be separated, and gently heated with concentrated hydrochloric acid; if it be sulphate of lead, it will dissolve, and the solution may be mixed with that from which the precipitate was originally obtained, but if it be insoluble in concentrated hydrochloric acid, it must be examined as a substance insoluble in water and acids.

3. It will be found convenient, in many cases, to test a small portion of this filtrate by adding a saturated solution of sulphuretted hydrogen, and boiling; for if no change be thus produced, it is of course unnecessary to treat the whole of the solution with that reagent.

It is requisite, especially if *arsenic* or *platinum* be present, to digest the liquid for some time at a moderate heat, after saturation with sulphuretted hydrogen, and to repeat the operation several times before these metals are completely separated.

Sulphuretted hydrogen often produces a precipitate of sulphur, arising from the presence of an oxidizing agent (*nitric acid, sesquioxide of iron, &c.*); this precipitate may be distinguished from all others by its white color, and by its remaining suspended in the liquid, and may be neglected altogether.

If the application of sulphuretted hydrogen to a yellow or red solution should change its color to a distinct green, from the reduction of *chromic acid*, it will be expedient to treat the whole of the solution with sulphuretted hydrogen, in order to effect the complete reduction.

4. The necessity of these operations will be apparent from the following remarks.

If the excess of sulphuretted hydrogen were not expelled from the filtrate before adding the nitric acid, the latter might give rise, by oxidation of the sulphur, to sulphuric acid, which would precipitate *baryta, strontia*, and perhaps even *lime*, as sulphates.

The nitric acid is added in order to oxidize any *oxalic acid* or *organic matter*, the former of which would carry down the *baryta, strontia*, and *lime* in the form of oxalates, upon the subsequent addition of ammonia, while the *organic matter* may interfere materially with the detection of the various bases. It is advisable to evaporate with nitric acid, even though the preliminary examination may not have indicated the presence of *oxalic acid* or of *organic matter*, since small quantities of these might easily escape detection.

The solution must, in any case, be evaporated to dryness, in order to convert any *silica* into the insoluble form, since the soluble modification might be easily mistaken for alumina.

The dry residue should not be strongly heated, if it can be avoided, since many of the oxides are redissolved with considerable difficulty after ignition.

5. An experienced eye will at once discern whether this residue consists solely of *silica*. Its color will show whether it is likely to contain any *sesquioxides of iron* or of *chromium* (which redissolve with great difficulty after strong ignition); if the flakes of *silica* be mixed with a white powder, this will proba-

bly consist of *sulphate of baryta* or of *strontia*, arising from the formation of sulphuric acid by the oxidizing action of the nitric acid. When the analyst is not satisfied that this residue consists of *silica* only, he should examine it as a substance insoluble in water and acids. (Table VIII.)

6. Chloride of ammonium is added to prevent the precipitation of *magnesia* (in any other form but that of phosphate) by ammonia.

The odor will show when an excess of sulphide of ammonium has been added. The mixture is boiled with this reagent in order to promote the decomposition of any *phosphate of iron*, &c., which might be precipitated by the ammonia.

7. Small quantities of the *oxalates* and *borates of the alkaline earths*, and of the *fluorides of the alkaline-earth-metals* may also be obtained in this precipitate, but need not be regarded, since their bases will always be detected in the filtrate, and the acids cannot be overlooked in the ordinary method of examination for acids.

8. Should this filtrate have a brown color, indicative of dissolved *sulphide of nickel*, it is evaporated until the excess of sulphide of ammonium is expelled, acidified with dilute hydrochloric acid, the precipitate thrown upon a filter, and examined together with that previously obtained.

9. The solution should not be boiled, since the chloride of ammonium might then decompose and dissolve the carbonates of the alkaline earths.

10. The presence of *soda* may be confirmed, and some idea of its quantity obtained, by decanting the supernatant liquid (containing excess of bichloride of platinum) from this crystalline precipitate, and evaporating it slowly down, in a watch-glass, placed upon a water-bath; the double chloride of platinum and sodium crystallizes in radiated needles, at the margin of the evaporated liquid.

The most delicate method of testing for *potassa* consists in evaporating the liquid, mixed with bichloride of platinum, to dryness, on a water-bath, and treating the residue with alcohol and a little water, when the crystalline double chloride of platinum and potassium will remain undissolved.

NOTES TO TABLE II.

1. *Boric, benzoic, and uric acids* are occasionally precipitated here, if the solution be pretty concentrated; the two former are dissolved by hot water, and the uric acid by heating with nitric acid.

2. Should this precipitate contain very much *chloride of lead*, it should be boiled with successive quantities of water, until a portion of the solution, decanted into a watch-glass, no longer crystallizes on cooling.

NOTES TO TABLE III.¹

1. When a large quantity of precipitate is at our disposal, it is convenient to

¹ Ansell has recently proposed a method for the detection of antimony and arsenic in the presence of tin, by which very small quantities of the two former metals may be detected. The sulphides precipitated from their solution in sulphide of ammonium are redissolved in nitro-hydrochloric acid, and the solution poured into a hydrogen-apparatus so arranged as to allow the gas to be washed with a dilute solution of acetate of lead, which absorbs any hydrochloric acid or sulphuretted hydrogen, and to pass the mixture of antimoniretted, arseniuretted, and free hydrogen into a test-tube half-filled with concentrated nitric acid, which converts the antimony and arsenic into antimonio and arsenic acids. After the gas has passed for about 15 minutes, the nitric solution is evaporated, the residue pretty strongly heated on a sand-bath, and treated with warm water, which dissolves the arsenic and arsenious acids; the aqueous solution is mixed with nitrate of silver, and ammonia very cautiously added, which causes a precipitate of arseniate or arsenite of silver. The residue of antimonio acid is dissolved in a very little nitro-hydrochloric acid, evaporated as far as possible, and tested with sulphuretted hydrogen for antimony. In order to detect the tin, the metallic precipitate is washed

treat a small portion, first, with sulphide of ammonium, and should any part of it be dissolved, to digest the whole of the precipitate with that reagent. In order to ascertain whether any portion of the precipitate has been dissolved by the sulphide of ammonium, the solution is tested with a slight excess of hydrochloric acid; if the precipitate thus obtained be white, or nearly so, it will consist of sulphur alone, and will show that none of the precipitate has been dissolved by sulphide of ammonium; but if the precipitate have a decided color, it must be inferred that some soluble sulphide is present.

The readiest method of detaching the precipitate from the filter is to open the latter very carefully, and to suspend it, with one hand, against the side of the funnel, whilst the sulphide of ammonium is dropped from the bottle, held in the other hand, in such a manner that each drop may carry down a certain quantity of the precipitate; in some cases it may be necessary to wash the precipitate of the filter with a fine stream of water from a wash-bottle.

2. Except where *copper* is present, very small quantities of *bisulphide of tin* can be left behind in this residue, so that if no copper be present, it is scarcely necessary to examine it for tin, unless very great accuracy be desired.

3. It is necessary that this precipitate be washed till all adhering chloride of ammonium is removed, since, otherwise, the *sulphide of mercury* might be partly dissolved on boiling with nitric acid.

4. *Sulphide of cadmium* is only found in this residue when *tin* is present.

5. In testing very small quantities, it is convenient to evaporate to dryness in a watch-glass, to add a single drop of dilute hydrochloric acid, then a few drops of water, to heat until the residue is dissolved, and then to fill the watch-glass to the brim with water; sometimes the milkiness does not appear till after two or three minutes.

6. This method of separating the sulphides of copper and cadmium was devised by Dr. Hoffmann: its success is perfect, if due care be taken to wash the precipitate thoroughly and rapidly, so that it may not be oxidised by exposure, and to filter quickly after boiling with sulphuric acid.

7. Both these precipitates are dried, ignited, together with their filters, in an open porcelain crucible; the ash fused with a little cyanide of potassium in a covered crucible; the fused mass boiled (in the crucible) with water, the reduced metal (*tin*, with traces of *antimony* and *copper*) allowed to subside, and the supernatant liquid poured off; the metallic particles are then washed, and heated to boiling with a little concentrated hydrochloric acid, the solution diluted with water, filtered, and chloride of mercury added; a white (or gray) precipitate of subchloride of (or metallic) mercury, appearing immediately, or nearly so, indicates the presence of *tin*.

8. No bisulphide of tin is found in this solution unless arsenic is present.

9. The precipitate should be removed, as far as possible, from the filter, and added, by small portions at a time, to fused nitrate of potassa, in a porcelain crucible; the filter (or that portion of it which is covered with precipitate) is cut into small strips, which are added separately, to the fused mass; when the whole has been added, the mass is emptied from the crucible into a small iron mortar or cup, where it is allowed to cool.

NOTES TO TABLE IV.

1. This precipitate is also liable to contain small quantities of the higher oxides of *manganese*, *nickel*, and *cobalt*, arising from the exposure of the ammoniacal solution to the air; hence the necessity of rapid filtration. Since manga-

off the zinc in the generating bottle, and boiled with hydrochloric acid, when chloride of tin is formed, which may be detected by the well-known reaction with chloride of mercury.

nese has been sought in another part of the precipitate, and cobalt and nickel would have been detected in the commencement, a serious error need scarcely be feared in this part of the examination.

2. In order to determine the state of oxidation in which the iron existed originally, it is necessary to test a portion of the aqueous or hydrochloric solution of the substance.

3. Since alumina itself is not very easily soluble in acetic acid, and might therefore be mistaken for phosphate of alumina, unless a sufficient excess of acid was added, it is advisable, if a precipitate be formed in this part of the table, to dissolve it in hydrochloric acid, to add an excess of potassa, and to separate the alumina by silicate of potassa (*see* p. 514), in order to ascertain the presence of phosphoric acid.

NOTES TO TABLE V.

1. The formation of an immediate precipitate, though conclusive as to the presence of *baryta*, does not negative that of *strontia*.

2. Since *baryta* and *strontia* are detected elsewhere, no examination of this precipitate is necessary.

3. The same remark may be applied to this precipitate of silicofluoride of barium.

4. Should any *baryta* be detected by this test, the evaporation with hydrofluosilicic acid and extraction with alcohol must be repeated.

EXAMINATION FOR ACIDS.

§ 354. PRELIMINARY EXAMINATION.

Experiment 1.—A small portion of the powder is heated in a glass tube open at both ends, and held obliquely.

I. Evolution of *sulphurous acid* indicates the presence of SULPHUR or of a SULPHIDE.

II. The formation of a *distinctly crystalline sublimate* is probably due to OXALIC or BENZOIC acid.

III. The various ORGANIC ACIDS will generally evolve *peculiar odors* or *inflammable vapors* in this experiment (*see* the Reactions of the Organic Acids).

Experiment 2.—A portion of the powder is heated nearly to boiling with concentrated sulphuric acid.¹

I. *Fuming acid vapors* are evolved: probable presence of HYDROCHLORIC, HYDROFLUORIC, or NITRIC acid; in the last case, the fumes will generally have a *brown color*.

The fumes should be distinguished, as far as possible, by the *odor*.

A moistened glass rod should be exposed to the fumes; if it be covered with a *white film* (silicic acid) the presence of a FLUORIDE may be inferred.

II. *Effervescence* takes place.

This may proceed from the evolution of *carbonic acid*, *carbonic oxide*, *sulphurous*, or *hydrosulphuric acid*, &c. (Approach the mouth of the tube to the flame.)

Sulphurous and hydrosulphuric acids will be recognized by their odor. The evolution of the former does not indicate with certainty its presence in the substance, since it might result from the deoxidation of the sulphuric acid.

¹ The application of heat must be avoided if a chlorate be present.

If the gas have not the odor of hydrosulphuric acid, and is capable of burning with a blue flame, it consists of carbonic oxide, which may result from the presence of: 1, a compound of CYANOGEN (when it would probably be accompanied by *hydrocyanic acid*); 2, TARTARIC acid (when carbonisation would take place); 3, CITRIC acid; or, 4, OXALIC acid.

III. A *yellow gas* having the odor of chlorine is evolved: presence of, 1, HYPOCHLOROUS acid; 2, CHLORIC acid (when the liquid would assume a deep yellow color); or, 3, a CHLORIDE, together with an oxidising agent (such as a nitrate, a metallic peroxide, &c.).

IV. *Brown, brown-red, or purple vapors*, are evolved: These may consist of one of the lower oxides of nitrogen (indicative of the presence of NITROUS or NITRIC acid), or of BROMINE or IODINE; the vapors should be tested with a little starch-paste on a glass rod; if the starch become *blue or purple* (whether at once or after diffusion through a little thin starch-paste), *iodine* is present; if a deep *orange yellow* color be imparted to the starch, *bromine* is present.

V. Hydrocyanic acid (recognized by its odor) is evolved: presence of HYDROCYANIC, HYDROFERRICYANIC, HYDROFERRICYANIC, or HYDROSULPHOCYANIC acid. In the last case, the hydrocyanic acid would be accompanied by *Hydrosulphuric acid*.

VI. ACETIC acid may be recognized by its odor.

VII. If the sulphuric acids become *very dark* in this experiment, we may infer the presence of non-volatile organic matters, *e.g.* SUGAR, STARCH, TARTARIC, GALLIC, or TANNIC acid; if it blacken but slightly, it may be due to an accidental impurity, and should be disregarded.

VIII. If *no change* has been produced by heating with sulphuric acid, the acid present will probably be found to be either SULPHURIC, PHOSPHORIC, BORACIC, or SILICIC; *uric, benzoic, and succinic acids*, also do not exhibit any characteristic behavior.

Exp. 3. Another portion of the original solid is heated with dilute hydrochloric acid.¹

I. *Effervescence*: presence of HYDROSULPHURIC, SULPHUROUS, or CARBONIC acid.

The evolved gas is tested: 1, for *hydrosulphuric acid* with paper moistened with solution of *acetate of lead*; 2, for *sulphurous acid* by its odor; and, 3, for *carbonic acid* by decanting the gas into *lime-water* (see p. 536).

In order to test for carbonic acid in the presence of sulphurous acid, a little bichromate of potassa may be added before treating with hydrochloric acid.

II. A gas having the odor of chlorine is evolved: presence of CHROMIC, NITRIC, CHLORIC, or HYPOCHLOROUS acid, or of some indifferent metallic oxide.

Hydrofluoric, hydrocyanic acid, &c., may also be evolved in this experiment.

PREPARATION OF THE SOLUTION TO BE EXAMINED FOR ACIDS.

§ 355. The solubility of the substance in different menstrua will have been ascertained in the examination for bases.

The aqueous solution is always examined separately for acids.

All the bases, except the alkalis and alkaline earths, should be removed from the solution to be tested for acids.

In general, the separation of the bases from the aqueous solution may be effected by adding a slight excess of carbonate of soda, boiling, and filtering of the precipitate.

In some cases, however, especially where organic matter is present, this method is not applicable, and recourse must then be had to some special method;

¹ This experiment may be omitted when the preceding one has not furnished any result.

thus, for example, lead and copper would be removed by sulphuretted hydrogen, iron by sulphide of ammonium, &c.

After the removal of the bases, the solution must be neutralized; if acid, by addition of ammonia in slight excess; if alkaline, by adding nitric acid, and gently heating, to expel any free carbonic acid. If an excess of nitric acid be added, it may be remedied by adding a slight excess of ammonia.

The method employed for dissolving the portion insoluble in water must be framed with reference to the results of the preliminary examination.

If the preliminary experiments have not indicated the presence of any *organic acid*, of *oxalic*, *hydrofluoric*, *hydrobromic*, or *hydriodic acid*, or of a *cyanogen* compound, the residue left by water may be dissolved in nitric or hydrochloric acid, and the solution tested for acids. Of course, the solution must always be effected with nitric acid, in order to test with nitrate of silver.

Should the preliminary examination have afforded grounds for suspecting the presence of any of the above acids, the residue left by water should be boiled with a strong solution of carbonate of soda, filtered, the filtrate neutralized with nitric acid (and ammonia) and tested for acids.

Any portion of the substance which is insoluble in water and acids must be examined by Table VIII.

GENERAL EXAMINATION FOR ACIDS.

§ 356. The analyst may often economize time in examining for acids, by reflecting upon the solubility of the various combinations of acids and bases; for instance, it would be obviously absurd to seek for sulphuric acid in a solution containing baryta, since sulphate of baryta is insoluble in water and acids; again, the insolubility of phosphate of lime would preclude the possibility of the presence of phosphoric acid (to any notable extent) in an alkaline solution containing lime.

In detecting the acids, the analyst proceeds, as in examining for bases, by a method of exhaustion, first proving, by the application of general reagents, that the acids present are members of certain groups, and afterwards having recourse to special tests, in order to distinguish the individual acids.

Since the presence of organic acids necessitates some important alterations in the method of examination, we have subjoined two tables, the latter of which is to be employed whenever the operator has reason (from the preliminary examination) to suspect the presence of organic acids.

The tables are followed by an enumeration of such special tests as are not included in them.

TABLE VI.—METHOD OF EXAMINATION FOR ACIDS, TO BE ADOPTED WHEN NO ORGANIC ACID IS PRESENT. (Note 1.)

<p>To a slightly ammoniacal solution, add CHLORIDE OF BARIUM.</p> <p><i>Precipitate may contain</i></p> <p>Sulphate of Baryta, } Phosphate " } (white) Borate " } Oxalate (Note 2.) } Fluoride of Barium } Chromate of Baryta (yellow). } (Note 3.)</p> <p>Add DILUTE HYDROCHLORIC ACID.</p>	<p>To a slightly ammoniacal solution, add CHLORIDE OF CALCIUM.</p> <p><i>Precipitate may contain</i></p> <p>Phosphate of Lime, } Borate of Lime (Note 2), } (white) Oxalate of Lime, } Fluoride of Calcium, } (Note 3.)</p> <p>Add ACETIC ACID.</p>	<p>To a neutral solution (Note 5), add NITRATE OF SILVER.</p> <p><i>Precipitate may contain</i></p> <p>Borate of Silver } Cyanide of Silver } Sulphocyanide " } Chloride " } Ferrocyanide " } Bromide " }</p> <p>(soluble)</p> <p>Phosphate of Silver } Chromate of Silver } Iodide } Ferrocyanide " } " (brown-red)</p> <p>Add NITRIC ACID.</p>	<p>To a neutral solution (Note 5), add SESQUICHLORIDE OF IRON.</p> <p><i>Precipitate may contain</i></p> <p>Phosphate of Iron (white)</p> <p>Sesquiferrous-oxide of Iron (blue). (Note 4.)</p>	<p><i>Solution, A deep red color Indicates</i></p> <p>Hydrosulphocyanic Acid.</p> <p><i>A dark greenish-brown color Indicates the presence of</i></p> <p>Hydroferricyanic Acid.</p>
<p><i>Undissolved,</i></p> <p>Sulphate of Baryta, } Baryta, } Presence of } Sulphuric } Acid. } Phosphoric, } Silicic, } Boric (Note 2), } Oxalic, or } Hydrofluoric Acid. } (Note 3.)</p> <p><i>Dissolved,</i></p> <p>The others.</p> <p>Boil, filter, and add AMMONIA in excess.</p> <p><i>Precipitate,</i></p> <p>Presence of</p>	<p><i>Undissolved,</i></p> <p>Oxalate of Lime } Fluoride of Calcium. }</p> <p>Test specially for Oxalic and Hydrofluoric Acids. (See pp. 536 and 537.)</p> <p><i>Dissolved,</i></p> <p>The others.</p> <p>Filter, if necessary, and add a drop of SESQUICHLORIDE OF IRON.</p> <p><i>Precipitate,</i></p> <p>Presence of Phosphoric Acid</p> <p>Confirm by a special test. (Note 4.)</p>	<p><i>Undissolved,</i></p> <p>Borate of Silver } Oxalate " } Phosphate " } Chromate " } (Note 5.)</p> <p><i>Dissolved,</i></p> <p>Chloride, Cyanide, Ferrocyanide, Bromide, Sulphocyanide, Iodide, and Ferricyanide of Silver.</p> <p>Wash, and heat gently with AMMONIA.</p>	<p><i>Undissolved,</i></p> <p>Borate of Silver } Cyanide of Silver } Sulphocyanide " } Ferrocyanide " }</p> <p><i>Dissolved,</i></p> <p>The others.</p>	<p>Add a slight excess of NITRIC ACID: agitate, that the precipitate may subside, wash by decantation, transfer to a porcelain crucible, dry, and heat to redness (when the Cyanogen-compounds are reduced to the metallic state).</p> <p>Boil the residue with DILUTE NITRIC ACID.</p>
		<p><i>Undissolved,</i></p> <p>Iodide of Silver } Sulphocyanide " } Ferrocyanide " }</p>	<p><i>Solution may contain</i></p> <p>Nitrate of Silver.</p> <p>Add HYDROCHLORIC ACID.</p> <p>If Silver be present, it indicates the previous presence of Cyanide or Ferricyanide of Silver.</p> <p>in the precipitate.</p>	<p><i>Residue may contain</i></p> <p>Chloride and Bromide of Silver.</p>

NOTES TO TABLES VI. AND VII.

1. The following acids are supposed to have been already detected and separated as they would be in following the systematic course.

Silicic, sulphurous, carbonic, hydrosulphuric, arsenious, and arsenic acids.

2. Since the *borates of lime and baryta* are soluble in ammoniacal salts, the non-formation of a precipitate is not to be regarded as establishing the absence of boracic acid.

3. Should the analyst have omitted to separate *arsenious and arsenic acids* from the solutions, they will be precipitated also by this reagent.

4. It must be remembered that the reactions of *arsenic acid* are very similar to those of *phosphoric acid*.

5. *A neutral solution is most easily obtained by carefully evaporating the ammoniacal solution till it is no longer alkaline to test-papers.*

6. When freshly precipitated, *cyanide of silver* is pretty soluble in nitric acid.

7. *Tartrates of baryta and lime* being soluble in ammoniacal salts, the absence of tartaric acid is not certain when no precipitate is produced.

8. The same remark applies to the *citrates*.

In order to test for tartaric and citric acids in solutions containing ammoniacal salts, these must be decomposed by evaporating the solution with repeated additions of carbonate of soda as long as any ammoniacal odor is perceptible; the excess of carbonate of soda may then be decomposed by a *very slight excess* of nitric acid, and the solution rendered alkaline by ammonia.

It is exceedingly difficult to distinguish tartaric and citric acids; more reliance must be placed in the judgment of the analyst than in any method of testing for these acids.

9. If a *fixed organic substance* be present in the solution, phosphate of iron will not be precipitated.

10. If a *fixed organic substance* be present in the solution, the deep red color will sometimes not be produced.

SPECIAL TESTS FOR INDIVIDUAL ACIDS.

PHOSPHORIC ACID.—Test with a *mixture of chloride of ammonium, ammonia, and sulphate of magnesia* (p. 533).

BORACIC ACID.—The *green alcohol flame* (p. 534).

HYDROFLUORIC ACID.—The production of *terfluoride of silicon* (p. 536).

HYDROCHLORIC ACID (in presence of hydrobromic acid).—The production of *chlorochromic acid* (p. 538).

HYDROBROMIC ACID (in presence of hydriodic and hydrochloric acids).—To a solution containing a slight excess of carbonate of soda, add a *mixture of solutions of sulphate of copper and sulphate of iron* (see p. 539), until the whole of the iodine is precipitated; to the filtered liquid, add a slight excess of *carbonate of soda*, again filter, and treat as described at p. 538.

HYDROCYANIC ACID.—The *Prussian blue test*; or *Liebig's test* with sulphide of ammonium (p. 540).

TANNIC ACID (as distinguished from gallic).—The production of a white precipitate with *dilute sulphuric acid* (p. 543).

BENZOIC ACID.—The separation of the crystalline acid on adding *hydrochloric acid* (p. 545).

SUCCINIC ACID (as distinguished from benzoic acid).—The production of a white precipitate on adding *alcohol*, *ammonia*, and *chloride of barium* (p. 545).

ACETIC ACID.—The *acetic ether* test (p. 545).

URIC ACID.—The *murexide* test (p. 544).

NITRIC ACID.—The test with *sulphate of iron* (p. 542); or with *copper* (p. 542).

CHLORIC ACID.—The behavior of the substance with *concentrated sulphuric* or *hydrochloric acid* (p. 542).

HYPOCHLOROUS ACID.—The production of a black precipitate with *sulphate of manganese* (p. 542).

TABLE VIII.—ANALYSIS OF SUBSTANCES INSOLUBLE IN WATER AND ACIDS (Note 1).

‡ 357.—I. *A small portion of the powdered substance is fused on CHARCOAL, with CARBONATE OF SODA and CYANIDE OF POTASSIUM, the mass being afterwards triturated and levigated; if any metallic particles be obtained, the subsequent fusion of the substance is performed in a porcelain crucible (in which case a special test for*

Alumina and for Silica (Note 2)

must be had recourse to); but if no metal be discovered, platinum foil, or a crucible of this metal may be employed.

The substance is very finely powdered, mixed with about four times its weight of CARBONATE OF POTASSA and SODA, and well fused over a gas-burner, or a blowpipe-flame, or in a coke-fire, and retained in a fused state for several minutes. The fused mass, when cool, is digested for some time in WATER, with the aid of heat.

Residue.

The residue is well washed, and dissolved in HYDROCHLORIC or NITRIC ACID (the former, unless the presence of

Silver or Lead

is suspected). (Note 3.) The solution is examined in the usual manner for all bases except the

Alkalies.

Solution,

Divided into two parts.

One part is acidulated with HYDROCHLORIC ACID (any precipitate (Silica) being disregarded), and examined as usual for bases (Note 4).

The other part is tested for acids in the usual manner.

(Note 5.)

II. EXAMINATION OF INSOLUBLE SILICATES FOR ALKALIES.

The finely powdered substance is mixed with three or four parts of HYDRATE OF BARYTA, and strongly ignited, in a crucible of platinum or porcelain, for about half an hour. The mass is digested in WATER acidulated with HYDROCHLORIC ACID, the solution evaporated to dryness, the residue heated with WATER, and BARYTA-WATER added to alkaline reaction; the solution is then filtered off, the Baryte separated by heating with AMMONIA and CARBONATE OF AMMONIA, the solution evaporated to dryness, the residue heated to expel ammoniacal salts, and tested, as usual, for

Potassa and Soda.

NOTES TO TABLE VIII.

1. Substances insoluble in water and acids are of comparatively rare occurrence, especially among artificial products.

The following are most frequently met with : *silica*, and the *silicates* of various metallic oxides ; the *sulphates of baryta and strontia* ; the *fluorides of barium, strontium, and calcium* ; *chloride, bromide, and iodide of silver* ; the insoluble modifications of *sesquioxide of chromium, alumina, binoxide of tin, and antimoniate of teroxide of antimony*.

2. In order to test specially for *alumina* and *silica*, the finely-powdered substance may be fused, in a *silver crucible*, with pure hydrate of potassa, the fused mass dissolved in water, the solution acidulated with hydrochloric acid and evaporated to dryness; the residue is then boiled with dilute hydrochloric acid, when the *silica* is left undissolved; the solution is mixed with excess of ammonia, which precipitates the alumina.

We may also test for *silica* by mixing the substance with fluoride of calcium, and heating with concentrated sulphuric acid, in a platinum crucible, when terfluoride of silicon will be evolved (see p. 536).

3. Should there be any portion undissolved by the acid, it will probably consist of *silica*, of charcoal, or undecomposed substance, and may generally be disregarded.

4. In general, the only bases which need be sought for in this solution are the oxides of tin and antimony, but alumina and even small quantities of lime and oxide of iron may sometimes be found in it.

5. It need hardly be observed that the organic acids, oxalic acid, &c., need not be sought for in the solution, since they would have been decomposed by the high temperature employed in the fusion.

QUALITATIVE ANALYSIS OF ALLOYS AND AMALGAMS.

§ 358. Since compounds belonging to this class always contain metals in an unoxidized state, they exhibit such a difference in their general behavior as to require a special method for their analysis.

The preliminary experiment on charcoal before the blowpipe-flame is the only one which generally yields any very satisfactory result; though it is sometimes useful to heat the alloy gently in a tube closed at one end, when *arsenic* and *mercury* will sublime.

The method employed for reducing alloys to a proper state of division, varies according to the hardness of the substance operated on.

Some alloys may be cut into small fragments with the scissors or shears, others may be broken in an iron or steel mortar; hard alloys which are not attracted by the magnet may be reduced by filing, the particles of steel being afterwards carefully removed with a magnet.

It is unsafe to granulate an alloy by fusing and pouring it into water, since its composition may be materially altered by such an operation.

The analysis of alloys and amalgams is conducted according to the following table.

TABLE IX.—ANALYSIS OF ALLOYS.

The alloy, as finely divided as possible, is boiled with moderately strong Nitric Acid (about 1 measure of the concentrated acid and 2 measures of water) till all action appears to have ceased; a considerable quantity of Water is then added, the whole boiled for some minutes, and filtered.

<p><i>Solution may contain</i> Cyanate of Potassa.</p>	<p>This residue is well washed, dried, and fused with about three parts of Cyanide of Potassium, in a covered crucible; the fused mass, when cool, is boiled with Water.</p>	<p><i>Residue may contain (Note 1)</i> Binoxide of Tin } <i>white or light gray.</i> Antimonious Acid } Gold } <i>dark gray or black.</i> Platinum }</p>	<p><i>Residue may contain</i> Tin, Antimony, Gold, and Platinum, • in the metallic state. Boiled with CONCENTRATED HYDROCHLORIC ACID, the undissolved metal allowed to subside.</p>	<p><i>Residue may contain</i> All other metals, of the nature of which does not preclude their existence in alloys. (Note 2.) This solution is analysed as usual.</p>
<p><i>Solution may contain</i> Chloride of Tin.</p>	<p>To this residue, and the remainder of the Hydrochloric solution, a few drops of Nitric Acid are added, and the whole boiled until all the metallic particles are dissolved.</p>	<p><i>Residue.</i></p>	<p>The solution is divided into three parts.</p>	
<p>A portion is decanted into a test-tube, diluted with Water, and tested with Chromate of Mercury: <i>White or gray precipitate.</i> Presence of Tin.</p>	<p>One small portion is tested for Gold with the Purp. of Cassius test.</p>	<p>Another part is tested for Platinum with Calceolans or Ammonia.</p>	<p>The largest portion of the solution is mixed with excess of sulphate of ammonia, and boiled for some time.</p>	<p><i>Solution may contain</i> Antimonio Acid, Orange precipitate, Presence of Antimony.</p>
<p><i>Solution may contain</i> Tin.</p>	<p>(If the precipitate be at all dry, from the presence of other sulphides, it may be boiled with Ammonia, the solution filtered, after addition of a little Sulphurated Hydrogen, and saturated with Hydrochloric Acid, when the</p>	<p><i>Pentarsenphide of Antimony will appear.</i></p>	<p>Acidified with Hydrochloric Acid, and treated with Sulphurated Hydrogen.</p>	

TABLE IX.—ANALYSIS OF ALLOYS.

NOTES TO TABLE IX.

1. If the alloy contain a *large proportion* of tin and a *little* arsenic, the latter is generally left in the residue, and must be sought for in another portion of the alloy by a special method.

2. The more-easily oxidizable metals, as potassium, sodium, magnesium, &c., are not generally sought in alloys. This solution may also sometimes contain small quantities of *platinum* and *antimony*, which must not be disregarded if it be the object of the analyst to detect these metals in particular. Even a considerable amount of platinum may be dissolved by nitric acid from an alloy containing much silver.

QUANTITATIVE ANALYSIS.

APPARATUS USED IN QUANTITATIVE ANALYSIS.

§ 359. The following is a list of such apparatus, not mentioned in the introduction to qualitative analysis, as will be required by the student in commencing this branch of chemistry.

A *platinum dish* capable of containing about four ounces.¹

A *platinum crucible* which will contain from four to six drachms. This crucible should be provided with a cover made in the form of a capsule.

Two or three *flasks* of German glass, containing about one pint. They should have a globular form, with flat bottoms, and lips slightly turned out, but without rim or spout; their necks should be rather narrow.

A *washing-bottle* for hot water.

One or two German *beakers* of about one quart capacity.

A pair of *watch-glasses*, to fit over each other.

One or two small stoppered *weighing-bottles*, two or three inches long.

A *wide test-tube*, three or four inches long, and one inch in diameter, provided with a smooth, sound cork.

Quantitative filtering-paper.

Several *glass plates* of various diameters, to fit over funnels and beakers; some of these should have a notch in the side to admit the stem of a funnel, or a glass rod.

A *water-oven* for drying filters, &c.

An *air-bath* (*Taylor's*).—A *water-bath*.—A *pipette*.—A small *glass siphon*.—A *balance* and *weights*.

A few observations on the above articles may prove of service to beginners.

The *quantitative filtering-paper* should not only possess the good qualities requisite in that used in qualitative analysis, but should leave a very small amount of ash. The paper should be cut into filters of different sizes, the two most useful diameters being about $5\frac{1}{2}$ and $7\frac{1}{2}$ inches. In order to determine the ashes of these filters, six are to be completely incinerated in a platinum crucible (*see p. 575*), and the weight of the resulting ash divided by the number of filters, in order to obtain a fair average. Good filters of the smaller size should not leave more than about 0.04 grain of ash. The Swedish paper leaves even less ash, but is very expensive and generally filters very slowly.

The *water-oven* should be made of copper, and provided with apertures to allow of the passage of a current of air; it is conveniently supported upon a tripod, over a gas-burner, or may be placed upon the sand-bath. A somewhat imperfect substitute for a water-oven may be made by immersing a beaker in an appropriate vessel of water, which is then heated to the boiling point; filters, however, are dried very slowly in this manner, since the removal of the moisture has to be effected by the irregular current of air in the beaker.

¹ This costly vessel is not absolutely indispensable; a Berlin dish or a platinum crucible may, with some sacrifice of time and convenience, be substituted for it in most cases.

Two *air-baths* will be found useful in the laboratory; one of these should be made after Taylor's pattern, with double bottom and sides, a tall chimney for promoting a current of air, which enters through apertures at the bottom of the bath, and a tube for introducing a thermometer. An apparatus of this kind serves for drying substances at regulated temperatures above the boiling point of water.

The other *air-bath* (to be used for evaporations, &c.) is a cylindrical vessel of tinned iron, 7 inches in height, and 9 in diameter, with a large hole close to the bottom, for the entrance of air. It may be covered with a sheet of porous paper, supported by a glass rod.

The *water-bath* is a pretty capacious vessel of copper or tin-plate, furnished with one or two sets of movable rings for various dishes.

The *balance* is, of course, an apparatus of the first importance to the quantitative analyst, and much care should be therefore bestowed upon its selection. For most practical purposes, a balance capable of turning with 0.01 grain, when loaded with 1,000 grains in each pan, will be found sufficiently accurate. For very accurate analyses, however, especially in organic chemistry, a balance is required which turns distinctly with 0.001 grain. A balance is also required which will carry about 5,000 grains in each pan, and yet turn with 0.1 grain. The best general balance will be found in one which is capable of bearing the above weight, and yet turns with 0.01 grain.

Our space will not permit us to enter into all the details necessary to be attended to in a good balance, but we think it advisable to lay particular stress upon the following points.¹

The balance should be inclosed in a tight glass case, to protect it from the action of air and acid fumes. It should be provided with a handle external to the case, by which the knife-edge may be brought down on to the agate plane. The beam should be graduated, so that the smaller weights may be placed upon it, on the principle of the steelyard, a little rider of gold wire being used for all the smaller weights, and shifted along the beam by means of a lever worked from the outside of the case. The pans should be suspended from knife-edge supports.

A small dish containing lumps of quicklime should be kept in the balance, to absorb moisture, &c.

OPERATIONS IN QUANTITATIVE ANALYSIS.

§ 360. Before proceeding to consider the methods actually employed for the determination of various substances, it may be well to describe some of the more important manipulations, upon the execution of which the success of the quantitative analyst will entirely depend.

WEIGHING.—In the process of weighing, the following cautions should be carefully attended to.

The knife-edge must not be allowed to fall suddenly on to the agate plane, but must be let down gradually and gently.

The fulcrum must not rest upon the planes during the removal or addition of a weight. The pans must not be allowed to swing to and fro. Accurate equilibrium is best indicated by a gentle oscillation of the beam, causing the index to deviate to the same extent on either side of the scale; in weighing by rest, an error may be caused by a particle of dirt upon the planes, &c. Of course the balance must be so placed that the beam is truly horizontal (indicated by a pendulum, or by spirit-levels), and should stand upon a firm table. The weights are always lifted with pincers, never touched with the fingers.

¹ These remarks refer to accurate scientific balances, rather than to such as may be employed for the practically useful analysis of ores, &c.

A crucible or dish must never be weighed while hot, for, independently of the currents of air produced in the balance-case, an error will be incurred from the circumstance that the proper amount of moisture will not have condensed upon the surface of the vessel until it has cooled to the temperature of the air. However, it is sometimes necessary, in the case of very hygroscopic substances, to weigh the crucible and its contents, when just on the point of cooling; in such a case, the weight of the empty crucible should be taken at the same temperature, when the second of the above causes of error is avoided.

Solid substances are usually weighed, when they are not very hygroscopic, in two watch-glasses, which are ground at the edges so as to fit closely together, or in covered crucibles. Sometimes, especially when the substance rapidly absorbs moisture, it is weighed in a small stoppered bottle.

Liquids should be weighed in stoppered bottles; weighing in open vessels is to be avoided in most cases, the loss from evaporation at the surface preventing accurate determination of the weight; a flask may sometimes be employed, but never a beaker.

In order to avoid the trouble of detaching each particle of a weighed solid from the vessel, it is usual to weigh the latter again afterwards, together with any particle of the substance which may have adhered to it.

Filters are weighed in wide tubes closed with corks; covered crucibles are sometimes conveniently substituted for these; or, in the case of large precipitates, a beaker covered with a glass plate.

MECHANICAL DIVISION.—The reduction of a substance to a proper state of division is far more important in quantitative than in qualitative analysis. The methods of effecting it have been pointed out at p. 84.

SOLUTION.—For quantitative analysis, substances are dissolved either in flasks or beakers; the latter are generally employed whenever ebullition is not necessary, since the residue left undissolved is so much more easily extracted from them than from flasks.

When the solution of a substance is attended with effervescence, an inverted funnel must be placed over the mouth of the beaker, with its rim just resting within that of the latter; this funnel may be slipped aside when a fresh quantity of the solvent is to be added, and serves to prevent any loss from spirting. When ebullition is absolutely necessary, the solution must be effected in a flask, in the mouth of which a small funnel is placed. If violent and prolonged ebullition is required (as in the complete oxidation of sulphides by nitric acid), a flask with a very long narrow neck is used.

When a Florence flask is employed for solution, it should be placed obliquely, to guard against spirting.

EVAPORATION.—Liquids which do not effervesce when heated may be evaporated in a dish, upon a sand or water-bath, or in an air-bath; the liquid must never be allowed to boil, or loss will surely result from the projection of drops of the liquid. Evaporation upon a water-bath, although often much slower than upon a sand-bath, is far safer, because the temperature never rises beyond 210°.

If evaporation be carried to dryness upon the sand-bath, it must be well watched towards the conclusion, since small portions of the solid are very liable to be thrown out with the bubbles of vapor.

In these cases it is always safer to employ the rough air-bath mentioned above, within which the dish is supported upon an iron ring, at about 2 or 3 inches from the bottom, and the evaporation may proceed, with occasional attention, for many hours, without danger of loss. A very convenient method of evaporating to dryness, consists in placing the dish upon an empty vessel over the flame, when heated air contained in the vessel communicates a perfectly uniform heat to every part of the dish. An old water-bath or common tinned iron pot may

be used. This plan is particularly applicable when a liquid is to be evaporated to dryness, and the residue strongly heated.

When liquids effervesce upon the application of heat, they must be evaporated in beakers or flasks as long as the effervescence continues, when they may be transferred to a dish, and evaporated as above.

Some care is necessary in transferring liquids from one vessel to another; the under part of the lip of the vessel to be poured from should be slightly greased with a little tallow, to prevent any drops of liquid from running down the side. The liquid is then slowly poured down a glass rod held obliquely against the lip. The vessel should be afterwards rinsed twice with distilled water.

If possible, it is better to avoid covering a dish with paper during an evaporation, since the process is considerably retarded by it, and the cover is liable to become wetted and break, when it may fall into the liquid below; however, if there be dust or ashes floating in the surrounding air, the dish may be covered with a piece of filter-paper, through which a glass rod is thrust so as to support it upon the dish; the paper should be renewed whenever there is danger of its breaking.

Some salts are very prone, when their solutions are evaporated, to creep up the sides of the dish, and, finally even over the edge of the latter, thus causing considerable danger of loss; this may generally be avoided by spreading a very thin film of tallow over the edge and inner rim of the dish.

When very large quantities of liquid are to be evaporated, the process is usually conducted in a large dish until the liquid has attained a small bulk, when it is transferred to a smaller dish, and the evaporation continued. Since, however, some loss is almost always incurred in transferring, it is better, whenever it is possible, to evaporate the liquid in successive portions in the small dish.

IGNITION.—The greatest care is requisite in the ignition of substances in order to prevent loss from spirting or decrepitation.

The process is generally conducted in dishes of porcelain or platinum, and sometimes in crucibles of these materials. When a substance is ignited in a dish, the latter should at first be heated in an air-bath, the temperature of which is gradually increased, until it is perfectly dry. During this process the dish is covered with a piece of platinum foil. The dish is then (still covered) gradually heated over the spirit-lamp or gas-flame until it has attained the proper temperature.

(Care must be taken before weighing a dish or crucible, that every particle of carbon which may have been deposited from the flame, is removed from the surface; this may be effected by a judicious application of a clear flame, or by wiping with a dry or damp cloth; in the latter case, the dish must be again heated before weighing.) Should any matter be found deposited upon the cover, the latter should be removed from the dish, carefully ignited, and replaced.

If a substance is ignited in a crucible, the latter is at first supported at a considerable distance above the flame, its cover loosely placed over it, and a moderate heat (gradually increasing) applied, until but little vapor is given off; the crucible, still partially closed, is then strongly heated, and, when the ignition appears to be completed, its cover is removed, the crucible placed obliquely, and the lid allowed to rest against its mouth so as to produce a current of air, which will remove the last traces of vapor, &c., or serve to oxidize any carbon or other substance present in the residue.

During ignition in porcelain crucibles, it is convenient to substitute platinum for those of porcelain, since the latter are apt to become coated with a film of difficultly-combustible carbon, which is not easily removed.

cases where there is much difficulty in burning off the last traces of carbon,

it is usual to direct a slow current of oxygen into the ignited crucible. This is done very easily from a gas-holder, to which is affixed a piece of flexible tube terminating in a glass nozzle.

PRECIPITATION.—Precipitation is always effected, if possible, in a beaker or precipitating-glass, since the precipitate is so much more easily removed from these vessels than from flasks. The solution is always well mixed with the precipitant by agitation, or by stirring with a glass rod.

When the precipitation is effected by a gas (*e. g.* by sulphuretted hydrogen), the latter is conducted in a slow stream into the solution contained in a precipitating glass (Phillips); it is advisable to place in the mouth of the glass funnel, the stem of which has been cut off so as to leave a short wide tube through which the delivery-tube of the sulphuretted hydrogen apparatus may pass.

If a precipitate subsides very readily, it may conveniently be separated from the greater part of the supernatant fluid by decantation, the clear liquid being removed either by cautiously inclining the vessel, or by means of a siphon or pipette, care being taken to avoid removing any of the precipitate.

It is, however, more usual to separate precipitates by filtration, in which process the following precautions will be found necessary.

The funnel is supported either in the mouth of a precipitating-glass, or on a retort stand; in the latter case a beaker should be placed beneath to receive the filtrate; a dish must not be used, as it is very liable to be overturned and to collect dust when uncovered. The stem of the funnel should be made to touch the side of the beaker, so that the liquid may run quietly down, and not splash. The beaker is covered with paper turned down over the edges, or with a notched glass plate. The funnel is also loosely covered with a glass plate. The funnel must be somewhat larger than the filter, which should be closely fitted to its sides, and then moistened with water. The supernatant liquid should first be poured upon the filter, the precipitate being left in the beaker, and afterwards rinsed out with water. The filter is never more than three-fourths filled with the liquid.

The last traces of precipitate are removed from the containing vessel either by mechanical or by chemical means; the former are to be preferred in most cases. A very convenient instrument for this purpose is a glass rod, one of the rounded extremities of which is covered with a very closely-fitting, well-joined cap of caoutchouc, with which the sides of the beaker or precipitating-glass are rubbed. To detach a precipitate from the sides of a flask, a long feather is used from which all the plumules have been stripped, except a little tuft at the end; this feather may be bent so as to reach any part of the interior of the flask. To remove a precipitate by chemical means, an appropriate solvent is employed, and the substance is then reprecipitated.

Great attention must be paid to the *washing of precipitates*, without which, of course, their exact weight can never be ascertained. Precipitates may be washed by decantation, by filtration, or by a combination of the two methods.

In washing the precipitate by decantation, it is repeatedly stirred up with the liquid with which it is to be washed, it is then allowed to subside, and the clear liquid decanted, either with or without a siphon (or pipette); the operation is repeated until the precipitate is completely washed.

Precipitates are washed, on a filter, by stirring them up with a (not too forcible) stream from the jet of the washing-bottle.

It is often advantageous to combine these two methods of washing, the precipitate being stirred up with the liquid to be used for washing, allowed to subside, the clear liquid decanted through the filter, and the precipitate again washed in the same way; it is finally thrown upon the filter, and the washing completed.

The commonest method of ascertaining whether a precipitate is perfectly

washed consists in evaporating a few drops of the washings upon a platinum-plate, when no considerable residue should be left; or sometimes a special test is applied to the washings when one can be found which is sufficiently delicate.

DETERMINATION OF THE WEIGHT OF PRECIPITATES.—Before weighing a precipitate, it must be freed from all adhering moisture, which may be effected either by mere drying or by ignition.

The precipitate is first partially dried by placing the funnel which contains it either in an air-bath, or at some distance above the sand-bath, where it may be supported upon an iron tripod. The subsequent process is varied according as the precipitate is to be weighed after drying at 212° , or after ignition. In the former case, the filter, with its contents, may be carefully folded within another filter, and placed in the water-oven; after about an hour, it may be removed from its paper case, and weighed in the wide tube closed with a cork; it is then replaced in the paper, and again heated in the water-oven for half-an-hour, when the weight is again determined, and so on until no further alteration in weight is perceptible. The filter may also be very conveniently dried in a porcelain crucible, or in a small beaker, which should be covered during the weighing, since dry filter-paper very rapidly absorbs moisture from the air.

When it is necessary to dry filters, in order to ascertain their weight before collecting the precipitate upon them, the operation is conducted in exactly the same manner.

If the precipitate is to be ignited, the operation proceeds as follows: A crucible of porcelain or platinum (according to the nature of the precipitate) is ignited, allowed to cool, and weighed. A sheet of smooth writing-paper is cut in half; one half-sheet is placed upon the clean table, the other half is then cut again in half; and the quarter-sheets placed side by side upon the half-sheet; this arrangement will be found the most convenient for collecting any stray particles of precipitate. The crucible is placed upon one of the quarter-sheets of paper, and as much as possible of the precipitate thrown into it, having been detached by gently crumbling the filter between the fingers. The filter is then doubled up several times in the direction of its length, and held at the top, either in a pair of platinum-tongs or by a stout wire of that metal coiled loosely round it. The flame of a spirit-lamp is now applied to the apex of the filter, which is held over the mouth of the crucible, and allowed to burn away, with occasional contact of the spirit-flame, until the ashes drop into the crucible. The latter is transferred to the other quarter-sheet of paper, and any particles which may have fallen around it are shaken into it. The crucible is now loosely covered, and heated first gently, and at some distance from the flame, and afterwards to redness; finally, the crucible is placed obliquely, with the lid resting against its mouth, until every trace of carbon has burnt away, which may be assisted, if necessary, by a current of oxygen.

§ 361. We shall now enter upon the consideration of the various methods employed for the simple determination of the bases and acids.

It would be impossible, within the limits of a practical manual, to describe all the methods which have been employed for the determination and separation of the various substances. It is therefore our intention merely to bring forward the best processes for determining the chief bases and acids, so that the student may practise them in the laboratory, and thus become acquainted with the general features of the quantitative estimation of each substance.

We shall also subjoin a number of the commonest examples involving the quantitative separation of those bodies which are most frequently associated, but the advanced student of this branch of analysis will soon perceive that his chief

OXIDE OF MERCURY.

§ 364. Mercury is most accurately determined either as *metal*, in the dry way, or as *sulphide*.

Determination as Metal.—In order to weigh the mercury in a metallic state, the following process is adopted:—

(About 50 grains of pure native cinnabar may be taken. The result should be within 0.5 per cent. of that obtained by calculation.)

A combustion-tube of hard glass, about 24 inches long, and $\frac{1}{2}$ inch in diameter, is drawn out over the lamp, at about 3 or 4 inches from one extremity, so as to leave a somewhat narrow open passage, which is then loosely plugged with asbestos; into the tube thus prepared, a layer of about 12 inches of a mixture of powdered quicklime with about $\frac{1}{2}$ of dry carbonate of soda is introduced.

The finely powdered substance (previously weighed) is placed in a shallow mixing-mortar, and intimately mixed, by degrees, with about 9 inches of the above mixture, transferred from the tube for that purpose. The mortar is rinsed out with a little more of the mixture, which is also introduced into the tube, and the latter is then filled up, to within about 6 inches of the top, with the mixture, which is covered with a loose plug of asbestos. This extremity of the tube is then drawn out in such a manner that it may form two bulbs, with a prolongation formed by the extremity of the original tube, which should be slightly bent up, to prevent the mercury from running out. The tube is then rapped horizontally on the table, so as to form a passage above the mixture, and is placed in a Liebig's combustion furnace; the hinder end of the tube is placed in communication with an apparatus for evolving dry carbonic acid gas, having a wash-bottle containing oil of vitriol, so that the operator may judge of the rapidity with which the gas is passing.

A slow stream (about 2 bubbles per second) of gas should be passed through the tube during the whole operation.

The combustion-tube is now surrounded throughout its whole length with red-hot charcoal, the fire being raised, at the end, to the highest temperature which the tube will sustain. All the mercury is then chased, with a spirit-lamp, into the bulbs, the carbonic acid apparatus disconnected, and that part of the tube which contains the mercury is drawn off and sealed with the aid of the blowpipe. The mercury is rinsed into a small weighed capsule or beaker, washed once or twice by decantation, dried on a water-bath, and weighed.

In the above determination it is recommended to employ perfectly dry materials, because the condensed moisture may give rise to considerable inconvenience. The stream of carbonic acid is employed to carry forward the whole of the mercury.

This process is very convenient and expeditious for the determination of mercury in its ores, but is far inferior in accuracy to the method of determining that metal as sulphide.

Determination as Sulphide.—(For practice, chloride of mercury may be taken. About 15 grains will suffice. The amount of mercury found should not differ more than 0.3 per cent. from that calculated.)

The actual method employed for the determination of mercury as sulphide varies according to the nature of the solution.

1. *The solution is free from nitric acid, and from any other substance which could precipitate sulphur from the sulphuretted hydrogen.*

The solution is acidified with hydrochloric acid, diluted with a considerable amount of water, and saturated with sulphuretted hydrogen (p. 574). The precipitate is collected upon a filter which has been dried and weighed (p. 575),

washed, till the washings have no longer an acid reaction, dried at 212°, and its weight determined (p. 575).

Calculation.

$$\begin{array}{l} \text{HgS} \quad \text{Hg} \\ \text{As } 116 : 100 :: \text{Weight of precipitate} : x \\ \quad \quad \quad x = \text{Weight of mercury.} \end{array}$$

2. *The solution contains no nitric acid, but some substance capable of oxidizing the hydrogen of the sulphuretted hydrogen.*

The precipitate obtained as above is washed off the filter into a flask, heated with hydrochloric acid, nitric acid being gradually added until the separated sulphur is yellow, the solution diluted with water, filtered, and treated as in case 3.

3. *The solution contains nitric acid.*

In this case, it is carefully evaporated with hydrochloric acid, on a water-bath, to expel the nitric acid, the solution largely diluted, and the mercury then precipitated by sulphuretted hydrogen, the rest of the determination being conducted in the usual manner.

When the suboxide and oxide of mercury are present simultaneously, and it is desired to determine their respective amounts, the former may be precipitated by hydrochloric acid, collected upon a weighed filter, washed, and dried at 212°.

OXIDE OF LEAD.

(For practice, about 25 grains of nitrate of lead, dried in a water-oven, may be employed. The result must be within 0.5 per cent. of the calculated amount of oxide of lead.)

§ 865. This oxide is usually precipitated either as *sulphate* or *oxalate*.

1. *Precipitation as Sulphate.*—The solution, which should not be very dilute, is mixed with a slight excess of dilute sulphuric acid, and with about twice its volume of alcohol. The precipitate of sulphate of lead, which is somewhat soluble in water, is allowed some hours to subside, collected upon a filter, and washed with diluted alcohol till the washings are no longer acid. It is then dried and ignited, in a porcelain crucible, with the precautions given at p. 575. After ignition, the ash is moistened with concentrated nitric acid, dried, again moistened with dilute sulphuric acid, dried, and gradually ignited. In this way, any reduced lead is reconverted into sulphate.

Calculation.

$$\begin{array}{l} \text{PbO.SO}_4 \quad \text{PbO} \\ 151.7 : 111.7 :: \text{Weight of precipitate} : x \\ \quad \quad \quad x = \text{Weight of oxide of lead.} \end{array}$$

In cases where the addition of alcohol is inadmissible, the solution must be precipitated with a considerable excess of dilute sulphuric acid; the precipitate, after standing for some time, is collected upon a filter, washed with water, till the washings are but slightly acid, and treated as before.

The presence of much free nitric acid prevents the complete precipitation of sulphate of lead; when this acid is present, therefore, in large quantity, the solution must be evaporated nearly to dryness before adding the diluted sulphuric acid.

2. *Precipitation as Oxalate.*—The solution under examination is mixed with oxalate of ammonia, and ammonia added in slight excess. The precipitate is collected on a filter, washed with water, till the washings leave no residue on evaporation, dried, ignited in a porcelain crucible, with the usual precautions,

and weighed. The ash is afterwards moistened with concentrated nitric acid, dried at a gentle heat, and again ignited, to reoxidize any reduced lead. The whole of the lead is thus obtained as oxide, into which form the oxalate is converted by ignition.

TEROXIDE OF BISMUTH.

(For practice, two determinations should be made in an aqueous solution of nitrate of bismuth; the results should correspond within, at most, $\frac{1}{10}$ of the teroxide of bismuth present.)

§ 366. Teroxide of bismuth is precipitated either as *carbonate* or as *ter-sulphide*.

1. *Precipitation as Carbonate*.—The teroxide of bismuth can only be precipitated in this form from solutions which contain no other acid but nitric, since if any sulphuric or hydrochloric acid be present, it will be carried down in the form of a basic salt, and cannot be removed by washing.

The solution is diluted with water (any precipitate being disregarded), mixed with excess of sesquicarbonate of ammonia, and gently heated for some time. The precipitate is collected on a filter, washed with water, dried, and afterwards treated in the same manner as the oxalate of lead. After ignition, it is pure teroxide of bismuth.

2. *Precipitation as Tersulphide*.—The solution is largely diluted with water acidulated with acetic acid, and saturated with sulphuretted hydrogen; the precipitate is collected upon a filter, and well washed; the filter is then perforated with a pointed glass rod, and the precipitate washed completely into a flask, where it is to be heated with moderately strong nitric acid (which may be previously warmed and poured over the filter, to dissolve the last traces of the precipitate), until completely decomposed. The solution is then diluted with water acidulated with nitric acid, filtered, the filter thoroughly washed with acidulated water, the solution evaporated, if necessary, to expel the greater excess of acid, and the bismuth precipitated as carbonate.

OXIDE OF COPPER.

(Crystallized sulphate of copper should be analyzed for practice, all adhering water being removed by pressure between blotting-paper. 20 grains are sufficient for analysis. The amount of oxide of copper obtained should not differ more than 0.3 per cent. from the calculated result.)

§ 367. Oxide of copper is precipitated in the form of *oxide* or *sulphide*, but is always determined as oxide.

1. *Precipitation as Oxide*.—The moderately diluted solution is heated nearly to ebullition, in a beaker, and mixed with an excess of solution of potassa (previously diluted with water). The mixture is digested for some time at a temperature approaching ebullition, the precipitate allowed to subside, collected on a filter of known ash, washed with boiling water, till the washings leave no residue on evaporation, dried, ignited in a porcelain crucible, with the usual precautions (p. 575), and weighed when just on the point of cooling (p. 572). The weighing should be executed as rapidly as possible, since oxide of copper is exceedingly hygroscopic.

2. *Precipitation as Sulphide*.—The solution, which must not contain a large excess of free nitric acid, is acidulated with hydrochloric acid, largely diluted with water, and saturated with sulphuretted hydrogen; as soon as this reagent ceases to produce any further precipitate, the latter is allowed to subside, rapidly filtered off, and washed with solution of sulphuretted hydrogen as long as the washings have a very acid reaction. When the washing is completed, the apex of the filter is perforated with a pointed glass rod, and the sulphide of copper

washed off, as far as possible, into a pretty capacious flask; the filter is then dried, incinerated as usual in a porcelain crucible, and the ash added to the contents of the flask; a quantity of concentrated nitric acid is now poured into the latter, a funnel placed in the mouth to prevent loss from spirting, and the mixture maintained in rapid ebullition, on a sand-bath, until the sulphur has separated in pure yellow fused globules. A considerable quantity of water is then added, the solution filtered off, the filter being washed until the washings are no longer tinged by sulphuretted hydrogen, and the copper precipitated as oxide.

DETERMINATION OF COPPER IN ORES.—This is effected by ascertaining the quantity of a standard solution of sulphide of sodium required to precipitate the whole of the copper as *oxysulphide*, $\text{CuO}, 5\text{CuS}$, from an ammoniacal solution.

The standard solution of sulphide of sodium is prepared by saturating a solution of soda with sulphuretted hydrogen, and afterwards adding an equal volume of soda-solution of the same strength.

In order to graduate the solution, about 10 grs. of pure copper (electrotype copper) are dissolved in nitric acid, the solution measured, and divided into two equal parts; one part is somewhat diluted with water, and mixed, in a beaker, with excess of ammonia; the solution is heated just to the boiling point, at which it is maintained whilst the sulphide of sodium is added, cautiously, from a burette, with frequent stirring, until the liquid has lost its blue color; of course, when the blue color begins to fade away, the sulphide must be very carefully added, drop by drop, till the exact point at which the color vanishes has been attained.

The result of this experiment is confirmed by operating upon the other portion of the copper-solution; and the number of measures of the sulphide of sodium required for 100 grs. of copper are then calculated from the mean result.

The standard solution should be of such a strength that 1000 gr. measures are required to precipitate 10 grs. of copper.

In order to determine the amount of copper in an ore, it is reduced to a fine powder, and about 10 grs. of it dissolved as far as possible, in nitro-hydrochloric acid; the solution (not previously filtered) is diluted with water, and mixed with a considerable excess of ammonia; it is then filtered, and treated exactly as directed above, the amount of copper being calculated from the number of measures of standard solution employed.

Since the sulphide of sodium is readily oxidized by exposure to air, it should be graduated afresh before every series of analyses.

The above method may be employed for the determination of copper in its alloys and salts.

It has been proved by experiment that none of the metals associated with copper in nature can interfere with this determination, except silver, mercury, cobalt, and nickel, the first of which can be easily removed by hydrochloric acid before applying the above method.

If zinc be present in the ore analyzed, it will be indicated by the formation of a white precipitate of sulphide on adding a little more sulphide of sodium after the whole of the copper has been precipitated.

OXIDE OF CADMIUM.

(For practice, about 15 grains of pure dry sulphide of cadmium may be analyzed. The result should be within 0.5 per cent. of the calculated amount of metal.)

§ 368. Cadmium is determined as *oxide* or *sulphide*.

1. *Determination as Oxide.*—The moderately diluted solution is heated nearly to ebullition, in a flask, and solution of carbonate of soda gradually added in excess.

The mixture is then boiled for a few minutes, the precipitate allowed to subside, collected on a filter, washed with hot water till the washings leave no residue on evaporation, dried, detached very carefully from the filter, which must be completely incinerated before being introduced into the porcelain crucible containing the precipitate, ignited, and weighed.

If ammoniacal salts be contained in the solution, the ebullition must be continued until, after a fresh addition of carbonate of soda, no ammonia can be perceived.

2. *Determination as Sulphide.*—The solution, which must be largely diluted, and not very strongly acid, is saturated with sulphuretted hydrogen, and allowed to stand for some time for the precipitate to separate. The sulphide of cadmium is collected upon a weighed filter, washed with water containing sulphuretted hydrogen, dried at 212° , and weighed.

If there exists in the solution any substance capable of precipitating sulphur from the sulphuretted hydrogen, the sulphide obtained as above must be dissolved in nitric acid, and the cadmium precipitated as oxide.

Calculation.

$$\begin{array}{l} \text{CdS} . \text{Cd} \\ 72 : 56 :: \text{Weight of Precipitate} : x \\ x = \text{Weight of Cadmium.} \end{array}$$

TEROXIDE OF GOLD.

(For the sake of practice, a solution of tetrachloride of gold may be analyzed by two different methods. The results should not differ by more than $\frac{1}{8}$ of the metallic gold found.)

§ 369. Gold is always determined in the *metallic state*.

1. The solution, which must not contain any free nitric acid, is acidified with hydrochloric acid, and mixed, in a porcelain dish, with a clear solution of sulphate of iron. The mixture is digested at a gentle heat for several hours, the precipitated metal collected on a filter, well washed, dried, and ignited.

2. The solution, which must, in this case also, be free from nitric acid, is mixed, in a beaker, with oxalate of ammonia, and a slight excess of hydrochloric acid; the mixture is heated until all the gold is precipitated (which may be ascertained by testing a trace, upon a watch-glass, with chloride of tin), the metal filtered off, washed, dried, and ignited.

Solutions of gold which contain free nitric acid must be evaporated once or twice, to a small bulk, with excess of hydrochloric acid, until the former acid is expelled; of course, the precipitation of metallic gold during the evaporation will not affect the determination.

BINOXIDE OF PLATINUM.

(Solution of the bichloride is analyzed for practice; the results of two determinations should not differ by more than $\frac{1}{8}$ of the metallic platinum.)

§ 370. Platinum, like gold, is determined in the *metallic state*.

The rather concentrated solution (which, if acid, should be nearly neutralized with ammonia) is mixed with an excess of solution of chloride of ammonium, and an equal volume of alcohol; the mixture is set aside for several hours, the precipitated double-salt collected upon a filter of known ash, washed with spirit of wine, dried, ignited, in a platinum crucible, and weighed. The precipitate should not be detached, but wrapped up in the filter, placed in the crucible, which is then loosely covered, and gently heated as long as any fumes are disengaged; the heat is then gradually raised, and the incineration completed as usual.

The residue is pure metallic platinum (together with the ash of the filter).

OXIDE AND BINOXIDE OF TIN.

(Two analyses of a solution of bichloride of tin may be made for practice. The results should not differ by more than $\frac{1}{10}$ of the metal present.)

§ 371. Tin is determined either in the form of *binocide* or *bisulphide*.

Determination as Binocide.—When the tin is in the metallic state, it is boiled with moderately concentrated nitric acid as long as any oxidizing action takes place; a considerable quantity of water is then added, the mixture digested for some time at a gentle heat, and the precipitate allowed to subside; the latter is collected upon a filter of known ash, well washed with hot water, dried, ignited, with all the precautions, in a porcelain crucible, and weighed; before weighing, it is generally advisable to reoxidize any reduced tin by moistening the ash with nitric acid, drying at a gentle heat, and afterwards strongly igniting.¹

If the tin be contained in solution, it may be converted into binocide, if not already existing in that form, by passing a few bubbles of chlorine gas; the solution is then introduced into a flask, diluted with water, mixed with a considerable excess of solution of sesquicarbonate of ammonia, and boiled for some time; the precipitated binocide of tin is collected upon a filter of known ash, washed with a solution of sesquicarbonate of ammonia (pure water washes it through the paper) till the washings are free from chloride of ammonium, dried, ignited, with precautions, and weighed.

Calculation.

$$\begin{array}{l} \text{SnO}_2 \quad \text{Sn} \\ 74 : 58 :: \text{Weight of precipitate} : x \\ x = \text{Weight of tin.} \end{array}$$

Determination as Sulphide.—In order to precipitate the tin as a sulphide, the solution may be diluted with water acidulated with hydrochloric acid, and saturated with sulphuretted hydrogen; the solution is digested for a length of time at a gentle heat, the precipitate collected upon a filter of known ash, well washed and dried; it is then detached, as far as possible, from the filter (which is incinerated in the usual way), and gradually roasted in a porcelain crucible, until it is entirely converted into binocide of tin; before the final ignition, a fragment of sesquicarbonate of ammonia should be placed in the crucible.

In some cases, when there is no substance present in the solution to precipitate sulphur from the sulphuretted hydrogen, and when the whole of the tin is present in the form of binocide, the bisulphide of tin, precipitated as above, may be collected upon a weighed filter, washed, dried at 212° , and weighed.

Calculation.

$$\begin{array}{l} \text{SnS}_2 \quad \text{Sn} \\ 90 : 58 :: \text{Weight of precipitate} : x \\ x = \text{Weight of tin.} \end{array}$$

When the oxide and binocide of tin are present in the same solution, and it is desired to ascertain their respective quantities, two weighed portions of the solution must be taken; in one of these the total amount of tin may be determined as above, and the other portion may be gradually added to an excess of a hot solution of chloride of mercury which has been mixed with hydrochloric acid; the precipitated subchloride of mercury is collected upon a weighed filter, well washed, dried, and weighed. From the weight of this precipitate the amount of oxide of tin present may be inferred.

¹ It is unsafe to attempt the determination of tin by evaporating its solution with nitric acid, since a portion is volatilized as bichloride.

Calculation.

$$\begin{array}{l} \text{Hg}_2\text{Cl}_2 \quad \text{SnO} \\ 235.5 : 66 :: \text{Weight of precipitate} : x \\ x : \text{Weight of oxide of tin.} \end{array}$$

TEROXIDE OF ANTIMONY AND ANTIMONIC ACID.

(About 20 grains of tartar-emetic may be analyzed for practice; the antimony should not differ more than 0.3 per cent. from the calculated amount.)

§ 372. Antimony is usually determined as *tersulphide* or *pentasulphide*, or in the form of *antimoniate of tetroxide of antimony* (*antimonious acid*).

1. *Determination as a Sulphide*.—If the solution contain only tetroxide of antimony, unaccompanied by antimonious acid, or by any substance capable of decomposing sulphuretted hydrogen, so as to give rise to separation of sulphur, it is diluted with water acidified with hydrochloric acid, and thoroughly saturated with sulphuretted hydrogen; after standing for some time, the precipitate is collected upon a weighed filter, well washed, dried at 212° , and weighed.

Calculation.

$$\begin{array}{l} \text{Sb}_2\text{S}_3 \quad \text{Sb} \\ 177 : 129 :: \text{Weight of precipitate} : x \\ x = \text{Weight of antimony.} \end{array}$$

If, however, the solution contained any antimonious acid, or some substance capable of separating sulphur from the sulphuretted hydrogen, the precipitate is weighed, together with the filter, a portion of it detached and projected into a flask, the filter with the adhering precipitate being again weighed to ascertain how much has been removed. The portion in the flask is now treated, gradually, with the most concentrated nitric acid (free from sulphuric acid), and boiled until the oxidation of the sulphur is complete. The greater excess of the nitric acid is boiled off, the solution largely diluted with water acidified with hydrochloric acid, filtered, and the sulphuric acid precipitated as sulphate of baryta, from the weight of which we may calculate the amount of sulphur, and if this be deducted from the weight of the original dry precipitate, we obtain that of the antimony present.

A convenient method of determining the antimony directly in the precipitate consists in dissolving it in hydrochloric acid, and subsequently determining the antimony in the filtered solution as antimonious acid.

2. *Determination as Antimonious Acid*.—The solution under examination (which must not contain any other fixed constituent) is mixed with a considerable quantity of nitric acid, and carefully evaporated to dryness in a weighed porcelain capsule placed upon a sand-bath, or in an air-bath; the residue is strongly ignited until its weight ceases to vary. If any sulphuric acid be present, a fragment of carbonate of ammonia should be placed in the capsule (which must then be loosely covered) before the final ignition.

Calculation.

$$\begin{array}{l} \text{Sb}_2\text{O}_3 \quad \text{Sb} \\ 161 : 129 :: \text{Weight of residue} : x \\ x = \text{Weight of antimony.} \end{array}$$

DETERMINATION OF ANTIMONY IN ALLOYS.

Since antimony is almost always associated with tin in alloys, its determination is attended with considerable difficulty, from the remarkable similarity which exists between the compounds of these metals. The simplest method of deter-

mining these two metals is that recommended by Gay Lussac. Both metals are dissolved in *aqua regia*, the solution diluted, and digested with a plate of pure zinc until the whole of the tin and antimony is precipitated; the weight of this precipitate having been determined, it is redissolved in hydrochloric acid, with addition of a little nitric acid, and the antimony precipitated from the diluted solution by a plate of tin, at a gentle heat; the precipitated antimony is collected and weighed, the tin being determined by difference. This method, however, is liable to error from several causes, and is only capable of yielding an approximation to the amounts of tin and antimony which are present.

ARSENIOUS ACID.

(Two determinations of arsenic may be made in a hydrochloric solution of arsenious acid; the amount of arsenic obtained should not differ by more than $\frac{1}{10}$ of its weight in the two determinations.

§ 378. Arsenious acid is generally determined as *terrasulphide* of arsenic.

The determination is conducted on the same principles and in exactly the same manner as in the case of antimony.

Calculation.

$$\begin{array}{l} \text{AsS}_3 \quad \text{AsO}_3 \\ 128 : 99 :: \text{Weight of precipitate} : x \\ x = \text{Weight of arsenious acid.} \end{array}$$

ARSENIC ACID.

(Two determinations may be made in a solution of arsenic acid.)

§ 374. This acid is weighed, either as pentasulphide of arsenic, or as arseniate of sesquioxide of iron, or arseniate of magnesia and ammonia.

1. *Determination as Pentasulphide of Arsenic.*—The solution is mixed with excess of ammonia, and colorless sulphide of ammonium added till the precipitate first produced (if any) is redissolved; acetic acid is then added in excess, the solution digested in a warm place until the odor of sulphuretted hydrogen has disappeared, the precipitate collected upon a weighed filter, well washed with water, dried, and weighed.

A portion of the precipitate is then shaken out of the filter (which is then again weighed to ascertain how much has been detached) into a large flask, and carefully treated with nitric acid of moderate strength; as soon as the action has somewhat moderated, heat is applied, and continued until the sulphur (if any) separates in pure yellow globules; the solution is then diluted with water, the separated sulphur collected upon a weighed filter, well washed, dried at 212° , and weighed. The sulphuric acid contained in the solution is determined as sulphate of baryta from the weight of which the amount of sulphur is calculated. If the sulphur be calculated for, and deducted from, the total quantity of the original precipitate, we obtain the amount of the arsenic.

2. *Determination as Arseniate of Sesquioxide of Iron.*—This method consists in dissolving a weighed quantity of pure iron in nitric acid, mixing the solution with that of arsenic acid, and precipitating by ammonia. The precipitate of basic arseniate of sesquioxide of iron is collected on a filter, well washed with hot water, dried, carefully ignited, having been very carefully detached from the filter, and weighed. The ignition should not be sudden, but gradual, so that the trace of ammonia in the precipitate may be volatilized at first.

The amount of sesquioxide of iron which the pure iron ought to yield is then calculated, and deducted from the weight of the precipitate, when the difference gives the arsenic acid.

3. *Determination as Arseniate of Magnesia and Oxide of Ammonium.*—The

solution is mixed with free ammonia, and a mixture of sulphate of magnesia, chloride of ammonium and ammonia added; the mixture is well stirred without touching the sides of the vessel, and allowed to stand for 24 hours; the precipitate of arseniate of magnesia and ammonia is collected upon a weighed filter, washed with water containing some free ammonia, dried at 212° , and weighed.

Calculation.

$$2 \text{ MgO} \cdot \text{NH}_3 \cdot \text{O} \cdot \text{AsO}_5 + \text{Ag} \cdot \text{AsO}_5$$

$$190 \quad : \quad 115 :: \text{Weight of precipitate} : x$$

$$x = \text{Weight of arsenic acid.}$$

In order to determine the respective amounts of arsenious and arsenic acid when both are present in the same solution, the total quantity of arsenic may be ascertained by precipitation as a sulphide from the mixture of the solution with ammonia and sulphide of ammonium, the sulphur being afterwards determined in the precipitate, as directed above.

Another portion of the solution is then mixed with hydrochloric acid, and colored blue with solution of indigo. Solution of chloride of lime of known strength (*see* Chlorimetry) is added from a burette until the blue color just vanishes; the number of measures of solution must be observed, and from the quantity of chlorine which they are known to contain, the amount of arsenious acid (now converted into arsenic acid) is calculated.

$$\text{Cl}_2 \quad \text{AsO}_5$$

$$71 : 99 :: \text{Amount of chlorine employed} : x$$

$$x = \text{Weight of arsenious acid.}$$

By deducting the amount of arsenic present as arsenious acid from the total quantity known to be contained in the solution, we may ascertain the weight of arsenic which is present in the form of arsenic acid.

ALUMINA.

(For practice, crystallized alum may be employed; the crystals should be coarsely powdered, and dried by pressure between blotting-paper. 30 grains will suffice for the determination of alumina. The result should not differ more than 0.3 per cent. from that obtained by calculation.)

§ 375. Alumina is always weighed as such.

The solution is mixed with a considerable quantity of chloride of ammonium, and a slight excess of ammonia; it is then heated for some time, and filtered; the precipitate is well washed with boiling water, till the washings are free from sulphuric acid, dried, ignited in a platinum crucible, and weighed.

The presence of fixed organic matters, it will be remembered, prevents the precipitation of alumina.

SESQUIOXIDE OF CHROMIUM.

(For practice, chrome-alum may be employed. 30 grains will suffice. The result must come within 0.3 per cent. of that obtained by calculation.)

§ 376. The sesquioxide of chromium is weighed in the pure state.

The solution, which must not be too concentrated, nor contain any fixed organic substance, is heated nearly to ebullition, and mixed with a very slight excess of ammonia. The mixture is maintained at a high temperature until the supernatant liquid appears colorless, when the sesquioxide is collected upon a filter, well washed with hot water, dried, ignited in a platinum crucible, and weighed.

SESQUIOXIDE OF IRON.

(Two determinations may be made in a solution of sesquichloride of iron; the results should agree within $\frac{1}{4}$ of the amount of sesquioxide present.)

§ 377. Sesquioxide of iron is weighed in the pure state.

Different processes are employed for the determination of sesquioxide of iron, according as the solution contains fixed organic matters (as tartaric acid) or not.

1. *In Solutions free from fixed Organic Matters.*—The solution is mixed with an excess of ammonia, and heated nearly to ebullition; the precipitate is collected upon a filter, well washed with hot water (till the washings are free from chloride of ammonium, which would cause a loss of iron during the subsequent ignition), dried, incinerated, in a platinum crucible, with the usual precautions, and weighed. In very accurate analysis, it is well to moisten the ash with nitric acid, to dry, and ignite again before weighing, in order to reoxidize any iron which may have been reduced.

2. *In Solutions containing fixed Organic Matters.*—The solution is rendered slightly alkaline with ammonia, and mixed with an excess of sulphide of ammonium; it is then digested for some time at a moderate heat, until the solution has a pure yellow color, when the precipitated sulphide of iron is collected upon a filter, and well washed with water containing sulphide of ammonium; the apex of the filter is then perforated with a glass rod, and the precipitate washed off into a flask placed below; the remainder of the precipitate is dissolved off the paper with warm dilute hydrochloric acid, in which the whole of the sulphide is then dissolved. The solution is heated till no smell of sulphuretted hydrogen is perceptible, boiled with nitric acid until the iron is peroxidized, and the latter metal is then determined in the solution as directed above.

Sesquioxide of iron is sometimes precipitated as succinate, for which purpose the solution is gradually mixed with dilute ammonia until a slight precipitate is produced, which does not redissolve entirely, even on application of a gentle heat. A perfectly neutral solution of succinate of ammonia is now added as long as any precipitate is formed, the solution gently heated, and allowed to stand for some time; the precipitated succinate of sesquioxide of iron is filtered off, washed, first with cold water, and afterwards with warm dilute ammonia (which removes a part of the succinic acid), dried, and ignited (with all the precautions given at p. 575) in a platinum crucible; before weighing, the ignited precipitate may be moistened with nitric acid, dried, and again ignited. In this way, pure sesquioxide of iron is obtained.

For the method of determining the sesquioxide of iron by means of permanganate of potassa, see analysis of iron ores.

OXIDE OF IRON.

(Crystallized sulphate of iron may be dried by pressure between blotting-paper, and analyzed for practice. 20 grains should be taken. The amount of oxide of iron found should be within 0.3 per cent. of the calculated quantity.)

§ 378. Oxide of iron is always weighed in the form of *sesquioxide*.

The solution of the compound under examination is heated with concentrated nitric acid (in a flask, or beaker covered with an inverted funnel) until no more red fumes are evolved; the solution then contains sesquioxide of iron, which may be determined as above.

Calculation.

$$\begin{array}{l} \text{Fe}_2\text{O}_3 \quad 2\text{FeO} \\ \text{As } 80 : 72 :: \text{Weight of precipitate} : x \\ x = \text{Weight of oxide of iron.} \end{array}$$

For the determination of oxide of iron by means of permanganate of potassa, see analysis of iron ores.

To determine the respective quantities of oxide and sesquioxide of iron present in the same solution, the total quantity of iron is first ascertained according to

the methods given above, and the amount of iron present in the form of oxide is then estimated by means of the standard solution of permanganate of potassa; if the weight of sesquioxide of iron corresponding to the iron present in the form of oxide, be calculated and subtracted from the total weight of sesquioxide previously obtained, the difference shows the quantity of sesquioxide of iron actually existing in the solution.

OXIDE OF COBALT.

(Two determinations may be made, for practice, in a solution of nitrate of cobalt, free from nickel. The results should not differ by more than (at most) $\frac{1}{10}$ of the oxide of cobalt obtained.)

§ 379. Cobalt is always weighed in the *metallic state*. It is sometimes precipitated as *oxide*, sometimes as *sulphide*.

1. *Precipitation as Oxide*.—The solution is mixed with an excess of a strong solution of potassa, and heated till the precipitate has acquired a brownish color; it is then collected upon a filter of known ash, well washed with hot water, and dried. The precipitate is detached, as far as possible, from the filter, carefully ignited, and weighed; the filter is incinerated and weighed separately.

A portion of the precipitate is introduced into a weighed bulb-tube of hard glass, which is then again weighed, and connected with an apparatus for evolving dry hydrogen; as soon as the apparatus is filled with hydrogen, a gradually increasing heat is applied to the bulb, which is ultimately raised to bright redness, and maintained at that temperature as long as any water is formed. The last traces of moisture are chased out of the tube with a spirit-flame, and the tube allowed to cool, while the hydrogen is still passing; the tube is then detached, held obliquely for some time to allow the displacement of the hydrogen by atmospheric air, and the weight of the metallic cobalt determined.

If the precipitate be not pure, or if the heat applied in its reduction be not sufficiently intense, it will be pyrophoric, oxidizing immediately on contact with air.

2. *Precipitation as Sulphide of Cobalt*.—The solution is mixed with some chloride of ammonium and an excess of ammonia; sulphide of ammonium is then added as long as any precipitate is formed, the sulphide of cobalt is washed with water containing sulphide of ammonium, the filter then perforated (so that the precipitate may be washed into a flask), and afterwards incinerated, the ash being added to the contents of the flask; these are then heated with concentrated nitro-hydrochloric acid, until the separated sulphur has a pure yellow color. The solution is diluted with water, filtered off, and the cobalt precipitated as oxide, which is afterwards reduced to the metallic state.

OXIDE OF NICKEL.

(For practice, two determinations may be made in the same solution. The results should be as accurate as in the case of cobalt.)

§ 380. This oxide is always weighed in the *pure state*, but is sometimes precipitated in the form of *sulphide*.

In order to precipitate the oxide of nickel, the solution is heated with an excess of potassa, nearly to ebullition. The precipitate is collected upon a filter, well washed with boiling water, dried, and ignited.

If the nickel is to be precipitated as sulphide, the solution is nearly neutralized with ammonia, and mixed with a slight excess of freshly-prepared colorless sulphide of ammonium. The precipitate is collected upon a filter, washed rapidly with water containing a little colorless sulphide of ammonium, and treated as in the case of sulphide of cobalt.

OXIDE OF MANGANESE.

(Pure crystals of sulphate of manganese may be employed. They should be powdered, dried between blotting-paper, and about 15 grains employed for analysis; the oxide of manganese should be determined within 0.8 per cent.)

§ 381. Oxide of manganese is generally determined in the form of *protoxydide* (Mn_2O_3). It is precipitated sometimes as *hydrate*, sometimes as *carbonate of oxide of manganese*; occasionally, the manganese is separated in the form of *sulphide*.

1. *Precipitation as Hydrate*.—The solution is heated nearly to boiling, and mixed with excess of solution of potassa; heat is then applied for some time, the precipitate filtered off, well washed with hot water, dried, and strongly ignited, with the usual precautions.

Calculation.

$$\begin{array}{l} Mn_2O_3, \quad 3MnO \\ 114.8 : 106.8 :: \text{Weight of precipitate} : x \\ x = \text{Weight of oxide of manganese.} \end{array}$$

2. *Precipitation as Carbonate*.—The process is conducted in quite the same way as in the preceding case, solution of carbonate of soda being substituted for the potassa.

3. *Precipitation as Sulphide*.—The solution is mixed with chloride of ammonium, an excess of ammonia is then added, and afterwards sulphide of ammonium; the precipitate is allowed to subside, the supernatant liquid filtered off, the precipitate subsequently collected upon the filter, and washed with water containing sulphide of ammonium. It is then washed off the filter (which is perforated for that purpose) into a flask, the adhering particles dissolved off with hydrochloric acid, in which the whole of the precipitate is afterwards dissolved; the solution is then heated until no more sulphuretted hydrogen is evolved, and the manganese then precipitated as carbonate.

OXIDE OF ZINC.

(For practice, sulphate of zinc may be employed. 10 or 15 grains may be taken. The result should be within 0.8 of the calculated amount.)

§ 382. Oxide of zinc is always weighed in the pure state, but may be precipitated either as *carbonate* or *sulphide*.

In order to precipitate the oxide of zinc as carbonate, the solution is treated exactly as in the case of cadmium (*see* p. 580). The filtrate must always be mixed with sulphide of ammonium, to ascertain if the precipitation be complete; should this reagent give rise to any considerable precipitate, it must be collected and treated as under.

When the zinc is to be precipitated as sulphide, it is mixed with excess of ammonia, and the subsequent process conducted as in the case of manganese. (*see* above).

BARYTA.

(Pure crystallized chloride of barium, dried between blotting-paper, may be employed for practice. 15 or 20 grains will be found sufficient. The result should not differ by more than 0.2 from the theoretical percentage, when the baryta is weighed as sulphate, nor more than 0.5 when it is obtained as carbonate.)

§ 383. Baryta is determined either as *sulphate* or *carbonate*.

1. *Determination as Sulphate*.—The solution is heated nearly to ebullition, dilute sulphuric acid added to complete precipitation, and the mixture allowed

to stand for some hours, until the precipitate has completely subsided. The supernatant liquid is then carefully decanted on to the filter (or it may even, in some cases, be drawn off by a siphon), and the precipitate then rinsed out on to the same filter with a moderately diluted hot solution of chloride of ammonium. The filter should never be filled more than half full, and each portion of liquid should be allowed to drain through before another is added. The addition of chloride of ammonium is necessary, to prevent the precipitate from passing through the pores of the filter.

If, notwithstanding, the filtrate should be turbid, it must be set aside, the particles allowed to subside, and again thrown upon the filter.

The sulphate of baryta is washed with hot water till the washings are free from sulphuric acid, dried, ignited, and weighed.

Calculation.

$$\begin{array}{l} \text{BaO.SO}_3 \quad \text{BaO} \\ 116.5 : 76.5 :: \text{Weight of precipitate} : x \\ x : \text{Weight of baryta.} \end{array}$$

2. *Determination as Carbonate.*—The solution, which should not be too concentrated, is mixed with excess of ammonia and sesquicarbonate of ammonia, and gently heated for a considerable time.

The precipitate is filtered off, washed with ammoniacal water, dried, ignited, and weighed. The ignition should not be too intense.

Calculation.

$$\begin{array}{l} \text{BaO.CO}_3 \quad \text{BaO} \\ 98.5 : 76.5 :: \text{Weight of precipitate} : x \\ x : \text{Weight of baryta.} \end{array}$$

STRONTIA.

(Pure nitrate of strontia may be taken. 20 grains should be employed. The result ought not to differ more than 0.5 per cent. from the theoretical amount when the strontia is precipitated as carbonate, nor more than $\frac{1}{8}$ of the whole amount of strontia when determined as sulphate.)

§ 384. 1. *Determination as Sulphate of Strontia.*—The solution, which must not be too dilute, is mixed with an excess of dilute sulphuric acid, and allowed to stand for several hours. The precipitate of sulphate of strontia is collected upon a filter, washed with water till the washings are no longer acid, dried, and ignited, the precipitate being very carefully detached from the filter.

If it be admissible to mix the solution, after adding sulphuric acid, with an equal volume of alcohol, and to wash the precipitate with dilute alcohol, the result will be much more accurate.

Calculation.

$$\begin{array}{l} \text{SrO.SO}_3 \quad \text{SrO} \\ 91.8 : 51.8 :: \text{Weight of precipitate} : x \\ x = \text{Weight of strontia.} \end{array}$$

2. *Determination as Carbonate.*—The process is conducted exactly as in the case of baryta.

Calculation.

$$\begin{array}{l} \text{SrO.CO}_3 \quad \text{SrO} \\ 73.8 : 51.8 :: \text{Weight of precipitate} : x \\ x = \text{Weight of strontia.} \end{array}$$

LIME.

(Pure calcareous spar, or even white marble, may be analyzed for practice. 10 to 15 grains should be taken. The amount of lime found should, if the specimen be pure, differ from the calculated quantity by not more than 0.3 per cent.; or two determinations should come within so much of each other.)

§ 885. Lime is generally precipitated as *oxalate*, and weighed as *carbonate*.

The solution is rendered ammoniacal and completely precipitated with oxalate of ammonia; it is gently heated until the precipitate has subsided, the latter collected on a filter (the supernatant liquid being poured through first), washed with hot water, dried, and very gently ignited, the filter being incinerated as usual. The mass is then drenched with a strong solution of sesquicarbonate of ammonia, dried in an air-bath, and weighed. This treatment is repeated until no further increase of weight is perceived (that is, till all the lime which had been caustified by ignition has been recarbonated).

Calculation.

$$\begin{array}{l} \text{CaO.CO}_2 \quad \text{CaO} \\ 50 : 28 :: \text{Weight of precipitate} : x \\ x = \text{Weight of lime.} \end{array}$$

MAGNESIA.

(Crystallized sulphate of magnesia may be analyzed for practice, 15 to 20 grains being employed. The result should not differ by more than 0.3 per cent. from the theoretical amount.)

§ 886. Magnesia is usually determined as *pyrophosphate*, being precipitated, for that purpose, in the form of *phosphate of magnesia and ammonia*.

The solution is mixed with enough chloride of ammonium to prevent precipitation by ammonia. An excess of the latter is then added, and afterwards a slight excess of phosphate of soda. The mixture is well stirred with a glass rod, which should not touch the sides of the beaker, and allowed to stand for at least twelve hours. The precipitate is then collected upon a filter, washed with water containing about one-eighth its volume of strong ammonia, until the washings leave no considerable residue on evaporation; the washed precipitate is dried, carefully ignited (p. 573), and weighed as pyrophosphate of magnesia.

Calculation.

$$\begin{array}{l} 2\text{MgO.PO}_2 \quad 2\text{MgO} \\ 112 : 40 :: \text{Weight of precipitate} : x \\ x = \text{Weight of magnesia.} \end{array}$$

POTASSA.

(Perfectly pure nitre, powdered and dried in a water-bath, may be employed for practice. Fifteen grains may be taken for determination by the first two methods, and five grains for the last. The amount of potassa found should be within 0.2 per cent. of that obtained by calculation.)

§ 887. Potassa is determined either as *sulphate of potassa*, as *chloride of potassium*, or as the *double chloride of platinum and potassium*.

1. *Determination as Sulphate of Potassa*.—The solution is mixed with somewhat more sulphuric acid than is thought necessary to combine with the whole of the potassa, and carefully evaporated to dryness in a platinum,¹ or porcelain capsule or crucible (which must be loosely covered towards the end of the operation) placed in an air-bath; the residue of sulphate of potassa is cautiously dried and

¹ Of course, the use of the platinum vessel must be avoided when nitric and hydrochloric acids are present together in the solution.

ignited. The ignition is afterwards repeated, when a fragment of sesquicarbonate of ammonia is placed in the crucible, to decompose any bisulphate of potassa which may have been produced. Since sulphate of potassa is very liable to decrepitate, great care must be employed in igniting it.

Calculation.

$$\begin{array}{l} KO.SO_3 \quad KO \\ 87 \quad : \quad 47 \quad :: \text{Weight of residue} : x \\ x = \text{Weight of potassa.} \end{array}$$

2. *Determination as Chloride of Potassium.*—The solution is mixed with excess of hydrochloric acid, evaporated to dryness,¹ as in the preceding case, cautiously heated to dull redness, and weighed.

Calculation.

$$\begin{array}{l} KCl \quad KO \\ 74.5 \quad : \quad 47 \quad :: \text{Weight of residue} : x \\ x = \text{Weight of potassa.} \end{array}$$

It need hardly be remarked that these methods are inapplicable when other fixed substances are present.

8. *Determination as the Double Chloride of Platinum and Potassium.*

If the acid present be volatile, the solution may be mixed with hydrochloric acid and excess of bichloride of platinum, and evaporated to dryness on a water-bath. The residue is then stirred up and digested with alcohol of about 80 per cent. (If there be a due excess of bichloride of platinum, the solution will have a distinct yellow color; if, however, this is not the case, it must be again evaporated to dryness, treated with water, some more bichloride of platinum added, and the evaporation repeated.) The residue of chloride of platinum and potassium is collected on a weighed filter, washed with spirit, dried at 212°, and weighed.

When a non-volatile acid is present, the solution, which must be pretty concentrated, is mixed with hydrochloric acid and bichloride of platinum, and a considerable quantity of strong alcohol added. The mixture is set aside for twenty-four hours, the precipitate collected on a filter, washed with spirit, dried, and weighed.

Calculation.

$$\begin{array}{l} KCl.PtCl_2 \quad KO \\ 244.2 \quad : \quad 47 \quad :: \text{Weight of precipitate} : x \\ x = \text{Weight of potassa.} \end{array}$$

SODA.

(Fifteen grains of perfectly pure, ignited carbonate of soda, may be employed for practice. The amount of soda obtained should be within 0.2 per cent. of the calculated quantity.)

§ 388. Soda is generally determined either as *sulphate of soda*, or as *chloride of sodium*.

Both determinations are effected in quite the same way as in the case of potassa.

Calculations.

$$\begin{array}{l} 1. \quad NaO.SO_3 \quad NaO \\ \quad \quad 71 \quad : \quad 31 \quad :: \text{Weight of residue} : x \\ 2. \quad NaCl \quad NaO \\ \quad \quad 58.5 \quad : \quad 31 \quad :: \text{Weight of residue} : x \\ \quad \quad \quad \quad x = \text{Weight of soda.} \end{array}$$

¹ A platinum vessel must not be used when nitric acid, &c. are present.

OXIDE OF AMMONIUM.

(Pure chloride of ammonium may be analyzed for practice; it should be dried in the water-bath. About 10 grains may be taken for the first method, the result of which should not differ by more than (at most) 0.5 per cent. from the calculated amount of oxide of ammonium. For the second method, 5 grains may be employed. The oxide of ammonium should be found within 0.2 per cent.)

§ 389. Oxide of ammonium is determined either as *chloride of ammonium* or as the *double chloride of platinum and ammonium*.

1. *Determination as Chloride of Ammonium*.—The compound under examination is placed in a capacious (pint) flask, furnished with a sound cork, bearing a long funnel-tube and a rather wide tube bent twice at right angles. The longer limb of this tube should be about 18 inches in length. A few ounces of water are poured upon the ammoniacal compound, so as to cover the extremity of the funnel-tube, through which an excess of solution of potassa is then poured, and the extremity of the delivery-tube allowed to dip about three inches below the surface of a mixture of concentrated hydrochloric acid with 2 volumes of water contained in a small flask. The evolution-flask is placed upon a sand-bath, and its contents heated to ebullition, at which point they are maintained for about half an hour. When the ebullition has been continued for this period, the apparatus is allowed to cool, and the receiving-flask then withdrawn. The solution of chloride of ammonium is carefully evaporated to dryness on a water-bath, in a platinum dish, and dried (on a water-bath) till the weight is constant. The dish is then gradually ignited till all chloride of ammonium is volatilized, and again weighed. The difference is the weight of the chloride of ammonium.

Calculation.

$$\begin{array}{l} NH_4Cl \quad NH_3O \\ 53.5 : 26 :: \text{Weight of Chloride} : x \\ x = \text{Weight of Oxide of Ammonium.} \end{array}$$

2. *Determination as the Double Chloride of Platinum and Ammonium*.—This is effected in exactly the same way as the analogous determination of potassa.

The result may be controlled by carefully igniting the precipitate, and determining the weight of the spongy platinum.

Calculation.

$$\begin{array}{l} NH_4Cl.PtCl_2 \quad NH_3O \\ 1. \quad 223.2 : 26 :: \text{Weight of precipitate} . x \\ \quad \quad Pt \quad NH_3O \\ 2. \quad 98.7 : 26 :: \text{Weight of metal} : x \\ \quad \quad x = \text{Weight of oxide of ammonium.} \end{array}$$

QUANTITATIVE DETERMINATION OF THE ACIDS.

SULPHURIC ACID.

(For practice, this acid may be determined in 15 grains of alum; the amount of sulphuric acid should agree, within 0.3 per cent., with that obtained by calculation.)

§ 390. Sulphuric acid is determined as *sulphate of baryta*.

The solution is acidified with hydrochloric acid, precipitated with chloride of barium, heated, in order that the precipitate may subside, and carefully filtered.

The sulphate of baryta is well washed with boiling water, until the washings are no longer rendered turbid by sulphuric acid, dried, ignited, and weighed.

When nitric acid is present, the solution containing the sulphuric acid must be largely diluted before precipitation, and the sulphate must be washed for a long time with boiling water.

Calculation.

$$\begin{array}{l} \text{BaO.SO}_3 \quad \text{SO}_3 \\ 116.5 \quad : \quad 40 \quad :: \text{Weight of precipitate} : x \\ x = \text{Weight of sulphuric acid.} \end{array}$$

PHOSPHORIC ACID.¹

(Pure crystallized phosphate of soda may be analyzed, after drying between blotting-paper. 30 grains may be employed for the first method, and half that quantity for the second.)

§ 391. Phosphoric acid may be determined as *phosphate of lead*, or as *basic phosphate of sesquioxide of iron*.

1. *Determination as Phosphate of Lead.*—The solution is acidified with acetic acid, and solution of acetate of lead added to complete precipitation; the precipitate (3PbO.PO_3) is filtered off, washed, dried, ignited with the usual precautions (especially removing the precipitate, as far as possible, from the filter), in a porcelain crucible, and weighed.

Calculation.

$$\begin{array}{l} 3\text{PbO.PO}_3 \quad \text{PO}_3 \\ 407.1 \quad : \quad 72 \quad :: \text{Weight of precipitate} : x \\ x = \text{Weight of phosphoric acid.} \end{array}$$

To control this determination, the precipitate may be dissolved in nitric acid, and the oxide of lead determined (*see p. 578*).

2. *Determination as Basic Phosphate of Sesquioxide of Iron.*—The solution (which must not contain any fixed organic matters) is mixed with a large excess of a solution of sesquioxide of iron of known strength; an excess of ammonia is then added, and the solution digested for some time at a gentle heat; if the precipitate originally produced by ammonia be not distinctly brown-red, enough sesquioxide of iron has not been added. The precipitate is collected on a filter of known ash, washed with hot water, dried, and very strongly ignited in a porcelain crucible. From the weight of the precipitate, the amount of the phosphoric acid is obtained by deducting that of the sesquioxide of iron which has been added.

The chief objections to this method are the necessity of employing a very large excess of sesquioxide of iron, and the circumstances that all the loss falls upon the phosphoric acid.

BORACIC ACID.

§ 392. Since there is no borate sufficiently insoluble to allow the boracic acid to be advantageously precipitated in that form, this acid is usually estimated by loss.

Free boracic acid may be determined in a solution which contains no other acid but nitric, by carefully evaporating with a weighed amount of pure oxide of lead, igniting, and weighing. The quantity of boracic acid is ascertained by deducting the known weight of the oxide of lead.

The same principle is applied in the determination of other free acids.

¹ Only the tribasic modification is here alluded to.

The compounds of boracic acid with soda may be analyzed by evaporating with an excess of pure sulphuric acid, until the latter begins to volatilize; the mass is then digested for 24 hours with absolute alcohol, and frequently agitated; the residual sulphate of soda is collected on a weighed filter, washed with alcohol till the washings are no longer acid, dried, ignited, and weighed.

SILICIC ACID.

(Pure quartz or sand may be employed for practice; they should be previously ignited; 10 grains will be amply sufficient for determination.)

§ 393. Silica is always determined in the *insoluble modification*.

If the substance under examination is decomposed by hydrochloric acid, it is exposed, in fine powder, to the action of the acid, and the solution afterwards evaporated to perfect dryness. The dry residue is heated for some time in the air-bath, moistened with concentrated hydrochloric acid, digested for some minutes at a gentle heat, a considerable quantity of dilute hydrochloric acid added, and the whole again heated until apparently nothing but silica remains undissolved. The latter is collected upon a filter of known ash, well washed with hot water, dried, ignited, and weighed.

The ignition of silica requires some special precautions, since, at a red heat, this substance is so very light that particles may easily be carried away by the slightest current of air. The safest method is to empty as much as possible of the silica into a crucible, in which it is ignited and weighed, the crucible being covered throughout the operation; the filter is then wrapped up and placed in a platinum crucible, in which it is very gradually heated, the crucible being loosely covered, until all the paper is charred, when the incineration may be completed in the usual manner.

If silver or lead be present, nitric acid may be used, in the above process, instead of hydrochloric.

If the compound under examination be not capable of decomposition by acids, it must be reduced to an impalpable powder, and intimately mixed, by means of a rounded glass rod, in a platinum crucible¹ placed upon a sheet of paper, with about four parts of pure carbonate of potassa and soda. A layer of the pure carbonates is placed above the mixture; the crucible should even now be only half filled. It is then loosely covered, and gently heated for some time, the heat being afterwards very gradually increased until it has attained to bright redness, and the mass is in perfect fusion, in which state it is retained for about an hour.

When cool, the crucible, and its cover if necessary, are placed in a pretty capacious beaker, and a few ounces of water poured over them, so that they may be entirely covered; they are allowed to digest for several hours in the cold, with occasional stirring, until the mass is completely dissolved out of the crucible; the latter is then removed with a glass rod or a pair of platinum tongs, and rinsed several times into the beaker, the contents of which are now to be largely diluted and carefully acidulated with hydrochloric acid. The solution is heated in the beaker (covered with a funnel) till no more bubbles of carbonic acid are evolved, when it may be transferred to a large dish, and the further process conducted exactly as in the case of compounds decomposed by hydrochloric acid.

In the above process, the heat is gradually applied to the crucible, in order that most of the carbonic acid may be expelled before the mass enters into perfect fusion; without this precaution, loss from spirting is inevitable.

It frequently happens that the fused mass is not entirely dissolved by water; it may, however, easily be known whether the decomposition has been complete,

¹ If easily reducible metals be present (as lead, silver, &c.), of course a platinum crucible cannot be employed. (See Analysis of Lead-glass.)

for otherwise, after addition of hydrochloric acid, fine gritty particles of undecomposed substance will remain at the bottom of the beaker; these should, if possible, be collected and weighed, their weight being deducted from that of the substance originally employed.

For the analysis of silicates by means of hydrofluoric acid, *see* Analysis of Glass.

SULPHUROUS ACID.

§ 394. This acid may be weighed in the form of *sulphate of baryta*.

The compound under examination is heated, in a flask, with fuming nitric acid until the oxidation is complete; the solution is then largely diluted with water, and the sulphuric acid precipitated as sulphate of baryta (*see* p. 592.)

Or the sulphurous acid may be oxidized by passing a slow stream of chlorine through the solution.

If sulphuric acid be present at the same time, its quantity must be determined before oxidation, and subsequently deducted from the total amount.

CHROMIC ACID.

(Bichromate of potassa, dried at 212° , may be analyzed for practice. 15 grains will be found sufficient. The percentage of chromic acid should be found within 0.3 per cent.)

§ 395. Chromic acid is determined either as *sesquioxide of chromium*, or as *chromate of lead*.

1. *Determination as Sesquioxide of Chromium*.—The solution is mixed with a slight excess of hydrochloric acid, a moderate quantity of alcohol added, and the solution heated until it has acquired a pure green color, and the excess of alcohol has evaporated.

Or the acid solution may be mixed with a strong solution of sulphurous acid, and heated until the color is changed to a pure green.

The sesquioxide of chromium is then determined in the usual manner (*see* p. 585).

Calculation.

$$\begin{array}{l} \text{Cr}_2\text{O}_3 \quad 2\text{CrO}_3 \\ 71.4 : 101.4 :: \text{Weight of precipitate} : x \\ x = \text{Weight of chromic acid.} \end{array}$$

2. *Determination as Chromate of Lead*.—The solution, if acid, is mixed with an excess of acetate of potassa, if neutral or alkaline, with an excess of acetic acid, and acetate of lead added to complete precipitation. The precipitate is allowed to subside, collected on a weighed filter, washed, dried at 212° , and weighed.

Calculation.

$$\begin{array}{l} \text{PbO.CrO}_3 \quad \text{CrO}_3 \\ 162.4 : 50.7 :: \text{Weight of precipitate} : x \\ x = \text{Weight of chromic acid.} \end{array}$$

HYDROFLUORIC ACID.

§ 396. Fluorides are usually analyzed by treating a weighed portion of the very finely powdered substance with concentrated sulphuric acid, and evaporating to dryness in a platinum vessel; the mass, when ignited, contains the bases in the form of sulphates, and if their respective quantities be determined, that of the fluorine may be inferred.

The hydrofluoric acid contained in a solution may be estimated as fluoride of calcium. The solution is mixed, in a platinum vessel, with excess of ammonia

and chloride of calcium; heat is then applied, and the mixture allowed to digest for some time, so that the precipitate may subside. The latter is collected upon a filter, washed, first with hot water, then with very dilute acetic acid, to remove any carbonate of lime, dried, ignited, and weighed.

Calculation.

$$\begin{array}{l} \text{CaF} \quad \text{F} \\ 39 : 19 :: \text{Weight of precipitate} : x \\ x = \text{Weight of fluorine.} \end{array}$$

CARBONIC ACID.

(For practice, the acid may be determined in 20 grains of pure ignited carbonate of soda, and in a similar quantity of calcareous spar or white marble. The percentage of carbonic acid should be found within 0.3 of that calculated.)

§ 397. Carbonic acid is either directly determined as *carbonate of lime* or indirectly as *carbonic acid*.

The direct determination as carbonate of lime is rarely executed except in the analysis of waters, to which we therefore refer for the plan of operation.

The determination of carbonic acid by loss is effected by decomposing the substance with sulphuric or dilute nitric or hydrochloric acid (one of the latter being used when the base forms a sparingly soluble compound with sulphuric acid), in an apparatus arranged in such a manner that nothing but dry carbonic acid can escape from it.

The apparatus of Fresenius and Will (described under Alkalimetry) is best adapted for this purpose. The operation of decomposing a carbonate with sulphuric acid is described in the same section.

When the carbonate contains a base which forms an insoluble or sparingly soluble compound with sulphuric acid (*e. g.* lime), the operation is conducted in a somewhat different manner.

A quantity of dilute nitric or hydrochloric acid (the former is preferable when no deoxidation is likely to ensue) is introduced into the generating-flask of the apparatus above alluded to, and the small weighed bottle containing the substance is suspended by a horsehair in such a manner that its orifice shall be a little above the level of the acid. The drying-flask is half filled with concentrated sulphuric acid. When the apparatus has been weighed, and proved to be perfectly tight, a quantity of acid is rinsed into the substance, and the agitation is repeated at intervals until the decomposition is completed; the generating-flask is then heated to about 100°, the wax stopper removed from the tube, and suction applied, through a vulcanized connector, to the tube of the drying-flask, so as to draw air slowly through the apparatus till it tastes no longer of carbonic acid. The apparatus is allowed to cool, and again weighed, when the loss indicates the carbonic acid.

OXALIC ACID.

§ 398. This acid is precipitated as *oxalate of lime*, or is indirectly estimated by conversion into carbonic acid gas.

In order to determine oxalic acid as oxalate of lime, the solution (which, if containing a free mineral acid, must be mixed with acetate of potassa) is slightly acidified with acetic acid, and completely precipitated with a mixture of chloride of calcium and acetate of potassa.

The precipitate is treated exactly as directed at p. 590.

Calculation.

$$\begin{array}{l} \text{CaO.C}_2\text{O}_4 \quad \text{C}_2\text{O}_3 \\ 50 : 36 :: \text{Weight of ignited precipitate} : x \\ x = \text{Weight of oxalic acid.} \end{array}$$

The indirect estimation is effected by converting the oxalic acid into carbonic acid, by treatment with binoxide of manganese and sulphuric acid in a Fresenius and Will's apparatus.

The details of the operation are given in the article upon the valuation of manganese-ores.

Calculation.

$$\begin{array}{l} 2CO_2 \quad C_2O_3 \\ 44 : 86 :: \text{Loss of the apparatus} : x \\ x = \text{Weight of oxalic acid.} \end{array}$$

HYDROCHLORIC ACID.

(About 10 grains of pure ignited chloride of sodium may be employed for practice; the percentage of chlorine found should be within 0.2 per cent. of the theoretical amount.)

§ 399. Hydrochloric acid is determined as *chloride of silver*.

The solution is acidulated with nitric acid, and nitrate of silver added, with constant stirring, as long as any precipitate is formed. The chloride of silver is then treated exactly as directed for the determination of silver (p. 576).

Calculation.

$$\begin{array}{l} AgCl \quad Cl \\ 143.6 : 35.5 :: \text{Weight of precipitate} : x \\ x = \text{Weight of chlorine.} \end{array}$$

Free chlorine may be converted into chloride of ammonium by treatment with excess of ammonia.

HYDROBROMIC ACID.

§ 400. This acid is determined as *bromide of silver*.

The solution, which, if alkaline, should be nearly neutralized with nitric acid, is precipitated with solution of nitrate of silver mixed with free nitric acid, gently heated, the precipitate allowed to subside, and the subsequent operations conducted as in the case of chloride of silver (p. 576).

Of course, if the bromide of silver be collected upon a filter (which should be avoided if possible), the greatest care must be taken to detach it before ignition. It would even be preferable to collect it upon a weighed filter, and to weigh it after drying at 212°.

Calculation.

$$\begin{array}{l} AgBr \quad Br \\ 188.1 : 80 :: \text{Weight of precipitate} : x \\ x = \text{Weight of bromine.} \end{array}$$

Free bromine may be converted into bromide of ammonium by treatment with excess of ammonia.

HYDRIODIC ACID.

§ 401. Hydriodic acid is determined as *iodide of silver*. To describe the process would be merely to repeat what has just been said respecting the determination of hydrobromic acid.

Calculation.

$$\begin{array}{l} AgI \quad I \\ 235.2 : 127.1 :: \text{Weight of precipitate} : x \\ x = \text{Weight of iodine.} \end{array}$$

Free iodine is to be converted into a mixture of iodide of potassium and iodate

of potassa by treatment with solution of potassa in slight excess. The solution is then nearly neutralized with nitric acid, an excess of nitrate of silver added, and, finally, a slight excess of nitric acid. The precipitate, which consists of a mixture of iodide and iodate of silver, may be treated exactly as if it consisted of the former only, since iodate of silver, when ignited, is converted into the iodide.

HYDROSULPHURIC ACID.

(For practice, pure tersulphide of antimony may be analyzed.)

§ 402. Hydrosulphuric acid (sulphur) is determined as *tersulphide of arsenic*, or as *sulphate of baryta*.

1. *Determination as Tersulphide of Arsenic*.—If the hydrosulphuric acid exists in solution, the latter is mixed with an excess of a rather dilute solution of arsenious acid in potassa. The mixture is then slightly acidified with hydrochloric acid, the precipitated tersulphide of arsenic collected on a weighed filter, washed with water, dried at 212° , and weighed.

But if the hydrosulphuric acid is to be determined in an insoluble substance, a weighed quantity of the latter is placed in a small gas-evolution flask, provided with a funnel-tube, and with a delivery-tube conveying the gas into a dilute solution of arsenious acid in potassa. Enough water is introduced to cover the extremity of the funnel-tube, the flask is placed upon a sand-bath, and when the apparatus is arranged, dilute sulphuric or hydrochloric acid is gradually added, and a gentle heat applied. At the termination of the process, a solution of carbonate of soda may be poured through the funnel-tube, when the evolved carbonic acid will expel the last traces of hydrosulphuric acid. The delivery-tube is carefully rinsed into the potassa-solution, the tersulphide of arsenic precipitated from the latter, by adding a slight excess of hydrochloric acid, collected on a filter, washed, dried at 212° , and weighed.

Calculation.

$$\begin{array}{l} \text{As}_2\text{S}_3 \quad \text{S}_8 \\ 123 : 48 :: \text{Weight of precipitate} : x \\ x = \text{Weight of sulphur evolved as hydrosulphuric acid.} \end{array}$$

2. *Determination as Sulphate of Baryta*.—For this purpose the sulphur is oxidized and converted into sulphuric acid, which may be effected either in the wet or in the dry way.

Oxidation in the wet way.—A weighed quantity of the finely powdered substance is introduced into a large flask,¹ and gradually drenched with the most concentrated nitric acid; when the first violence of the action has abated, heat is applied, and continued until either the whole of the sulphur is dissolved, or until that portion which has resisted oxidation has separated in the form of pure yellow globules (which must be collected upon a weighed filter, washed, dried in a water-bath, and weighed). The solution is now largely diluted with water, the sulphur filtered off, and the sulphuric acid determined in the filtrate according to the method given at p. 592.

In some cases it is advantageous to add, from time to time, a few grains of chlorate of potassa, in order to complete the oxidation.

In the above process, hydrochloric acid, with gradual addition of chlorate of potassa, is sometimes employed for oxidation.

Oxidation in the dry way.—The finely powdered substance is introduced into a porcelain crucible, placed upon a sheet of paper, and intimately mixed, by means of a glass rod, with three parts of pure nitre and three parts of dry car-

¹ At the warehouses for chemical apparatus, there are large green globular flasks with very long necks, which are peculiarly adapted for sulphur determinations.

bonate of soda, in fine powder. The mixture is gradually heated in the covered crucible until the oxidation is judged to be complete. When cool, the fused mass is digested with water (the crucible being placed in a beaker or dish, and water poured over it), at a gentle heat, until it is entirely dissolved out; the crucible is then removed and rinsed into the solution, which is to be passed through a filter, the residue being washed with hot water till the washings are free from sulphuric acid.

The solution is then acidulated (avoiding loss by effervescence) with hydrochloric acid, and the sulphuric acid precipitated as sulphate of baryta.

Calculation.

$$\begin{array}{l} \text{BaO.SO}_3 \text{ S} \\ 116.5 : 16 :: \text{Weight of precipitate} : x \\ x = \text{Weight of sulphur.} \end{array}$$

Since the methods of determining cyanogen and its compounds are involved in the history of that group of substances, we defer their consideration to a subsequent portion of this work.

NITRIC ACID.

§ 403. This acid is almost always determined indirectly.

1. The substance (in a perfectly dry state) is very finely powdered, and mixed, in a platinum crucible, with two or three parts of perfectly anhydrous borax. The crucible is weighed, and gradually heated until the mass is in a state of tranquil fusion; the loss of weight indicates the amount of nitric acid.

2. A weighed quantity of the substance (which must be free from chlorides) is dissolved in a little water, and introduced into a tubulated retort, connected, by means of an air-tight cork, with a quilled receiver, the tube of which dips into a strong solution of hydrate of baryta contained in a flask. A slight excess of pure, somewhat dilute, sulphuric acid is then added to the solution in the retort, which is then distilled to dryness at a moderate heat.

The solution in the flask is then treated with a few bubbles of carbonic acid, so that the latter may be in slight excess. The liquid is heated, to expel all excess of carbonic acid, and filtered, the precipitated carbonate of baryta being well washed. The baryta in the filtrate (which must be perfectly neutral) is then determined as sulphate.

Calculation.

$$\begin{array}{l} \text{BaO.SO}_3 \text{ NO}_3 \\ 116.5 : 54 :: \text{Weight of precipitate} : x \\ x = \text{Weight of nitric acid.} \end{array}$$

CHLORIC ACID.

§ 404. Chloric, like the preceding acid, is determined indirectly.

1. The dry compound may be ignited until the chlorate is converted into a chloride, and the amount of chloric acid calculated from the loss of oxygen. This determination may, of course, be controlled by an estimation of the chlorine.

2. The chloric acid in a solution may be liberated by sulphuric acid, and deoxidized with sulphurous acid; it may then (after expelling the excess of sulphurous acid by a gentle heat) be precipitated and weighed as chloride of silver.

For the determination of *hypochlorous acid*, see the article on Chlorimetry.

The quantitative determination of the *organic acids* falls within the province of organic chemistry.

QUANTITATIVE ANALYSIS; SPECIAL METHODS.

IN entering upon the complete analysis of substances, the student will find it advantageous to attend to the following cautions.

A quantitative analysis, to be successful, must be executed as rapidly as possible, but not hurriedly.

The analyst must not shrink from operations because they are tedious, or involve a great deal of weighing, but must have regard chiefly to accuracy, at any sacrifice, only adopting a shorter method when he has proved by experiment that its results will bear comparison with those obtained by the process which it is intended to supersede.

It is much better, though perhaps less strictly scientific, when there are many constituents to be determined in a substance, to employ separate portions, rather than to attempt to estimate them all in the same quantity of material.

CHLORIDE OF SODIUM.

NaCl.

§ 405. The *chlorine* is determined in one portion according to the method given at p. 597.

Ten grains of ignited chloride of sodium may be employed for the determination of the *sodium* as sulphate of soda, which is effected according to § 388.

It is customary, in quantitative analysis, to calculate the weight of each constituent upon 100 parts of the substance analyzed. In order to illustrate the calculation of the composition of a substance experimentally and theoretically, we cite an analysis of chloride of sodium:—

Amount employed for determination of chlorine = 10 grs.

Chloride of silver obtained = 24.51 grs.

$$\begin{array}{l} \text{AgCl} \quad \text{Cl} \\ 143.6 : 35.5 :: 24.51 : x \\ x = \frac{35.5 \times 24.51}{143.6} = 6.059 = \text{amount of chlorine found.} \end{array}$$

$$\begin{array}{l} \text{NaCl} \quad \text{Cl} \\ 10 : 6.059 :: 100 : x \\ x = \frac{6.059 \times 100}{10} = 60.59 = \text{percentage of chlorine found.} \end{array}$$

Amount employed for determination of sodium = 10 grs.

Sulphate of soda obtained = 12.13 grs.

$$\begin{array}{l} \text{Na}_2\text{O} \cdot \text{SO}_3 \quad \text{Na} \\ 71 \quad : \quad 23 :: 12.13 : x \\ x = \frac{12.13 \times 23}{71} = 3.929 = \text{amount of sodium found.} \end{array}$$

$$\begin{array}{c} \text{NaCl} \quad \text{Na} \\ 10 : 3.929 :: 100 : x \end{array}$$

$$x = \frac{3.929 \times 100}{10} = 39.29 = \text{percentage of sodium found.}$$

	Found.	Calculated.
Sodium	39.29	39.32
Chlorine	60.59	60.68
	99.88	100.00

CRYSTALLIZED PHOSPHATE OF SODA.



§ 406. The crystals should be coarsely powdered, and pressed between blotting-paper.

Determination of Water of Crystallization (24Aq).—About 20 grs. of the salt are placed in a pretty large crucible and dried in an air-bath, at a gradually increasing temperature, which must not exceed 580° F. (304°.5 C.). The desiccation is continued till the weight ceases to vary.

Determination of Water of Constitution (HO).—The dry residue is carefully ignited to full redness till its weight is constant.

Determination of Phosphoric Acid.—About 30 grs. of the crystals are dissolved in water, and the phosphoric acid precipitated as phosphate of lead (*see* p. 592).

Determination of Soda.—The filtrate and washings from the precipitated phosphate of lead are saturated with sulphuretted hydrogen, to precipitate the excess of lead as sulphide, which is then filtered off; the solution is evaporated to a small bulk in a beaker, transferred to a weighed (platinum) dish, mixed with excess of hydrochloric acid, and the soda determined as chloride (*see* p. 591).

HEAVY-SPAR.



§ 407. Any traces of water existing in the mineral may be expelled by ignition.

The mineral is reduced to a very fine powder, and about 15 grs. are intimately mixed with four times their weight of dry carbonate of potassa and soda (perfectly free from sulphuric acid), in a platinum crucible. The mixture should be effected with a warm glass rod; the crucible, which must not be more than, at most, three-parts filled, is heated, either over a good gas-burner or in a coke-fire (being then imbedded in magnesia), until the mass is perfectly fused, in which state it is retained for about an hour. When cool, the crucible is placed in a beaker, and digested with water at a moderate heat till the mass is completely disintegrated; the crucible is then removed with a glass rod or platinum tongs, and well rinsed into the beaker; the contents of the latter are filtered off, and the residue washed with hot water till the washings are perfectly free from sulphuric acid.

Determination of the Baryta.—The carbonate of baryta is placed, together with the filter, in a beaker, a considerable quantity of water poured over it, and hydrochloric acid in excess gradually added (a funnel being inverted over the beaker to prevent loss). The whole is then heated, when it should give a clear solution, which is poured off through a filter, in order to separate any flocks of paper, and the baryta determined in it as sulphate (p. 588).

Of course, both filters must be washed with hot water, till the washings are quite free from baryta.

Should the hydrochloric solution be milky, it is a proof that the decomposition

The loss of weight which the limestone has suffered in this process indicates the amount of water present; the determination, however, is not perfectly accurate, since the loss will be increased by the expulsion of the carbonic acid from the carbonates of iron and manganese, and by that of the organic matter; another source of inaccuracy is the conversion of the oxides of iron and manganese into higher oxides. However, the determination will be found sufficiently accurate for practical purposes.

Determination of Clay, Sand, Lime, Magnesia, and Iron.—About 100 grains of the powdered limestone are placed in a tall beaker covered with an inverted funnel to prevent loss from spitting, and about two ounces of water added; dilute hydrochloric acid is then added by small portions at a time, till all effervescence has ceased; the beaker is gently heated on a sand-bath, the residue allowed to subside, and collected on a filter of known ash; this residue is washed with hot water till the washings are no longer acid (these being mixed with the filtrate), dried, carefully incinerated, the ash moistened with nitric acid (to reoxidize any oxide of iron), dried, ignited, and weighed. After deducting the ash of the filter, we have the weight of the clay and sand contained in the limestone.

The proportions of these two ingredients may be judged of to some extent from the physical properties of the residue, since the sand would be gritty to the touch; or they may be roughly separated by suspension in water, when the particles of clay may be washed away, leaving the sand at the bottom. In order, however, to determine accurately the quantities of silica and alumina contained in this residue, from 10 to 20 grains of it, in a state of impalpable powder, should be mixed, in a platinum crucible, by means of a glass rod, with about 4 times its weight of carbonate of potassa and soda, and fused, by a gradually increasing heat, over a gauze burner or Argand spirit-lamp; after the mass has been retained in fusion for about half an hour, the crucible is allowed to cool, placed in a beaker (with inverted funnel), covered with water, and heated, with constant stirring, till the mass is, in great measure, disintegrated; hydrochloric acid is then added, by degrees, till it produces no more effervescence; the beaker is again placed on the sand-bath for some time, till no more bubbles of carbonic acid escape, the crucible removed (and well washed), and the contents of the beaker carefully evaporated to dryness in a porcelain dish; the residue is well dried, and mixed into a paste with concentrated hydrochloric acid—a little water added, the mixture heated for some minutes, more dilute hydrochloric acid added, the digestion continued for half an hour, and the solution filtered from the undissolved silica, which is well washed, dried, ignited, and weighed. The filtrate from the silica is mixed with excess of ammonia which throws down the alumina, to be washed, dried, ignited, and weighed.

The solution originally filtered from the clay and sand should be carefully measured or weighed.

About $\frac{1}{2}$ of this solution is mixed with a little concentrated nitric acid, and heated nearly to boiling (to peroxidize the iron); it is then allowed to cool, and mixed with excess of ammonia; the mixture is gently heated for a few minutes, and the precipitate collected, washed, dried, ignited, reoxidized with nitric acid, and weighed. Its weight represents that of the sesquioxide of iron (together with small quantities of silica, alumina, and sesquioxide of manganese, the two former of which render the precipitate of a lighter, and the latter, of a darker color than pure sesquioxide of iron) contained in the amount of limestone corresponding to the portion of solution employed.

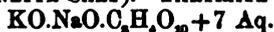
The filtrate from the sesquioxide of iron is mixed with oxalate of ammonia as long as any precipitate is formed, the solution heated, the precipitated oxalate of lime treated as directed at p. 590; the filtrate and washings being set aside for the following determination. Since the lime is weighed in the form of car-

of the sulphate of baryta was not complete. A true result may still be obtained by collecting the undecomposed sulphate upon another filter, incinerating the two filters after well washing, and deducting their ashes, when the weight of the undecomposed sulphate will be obtained, and may be subtracted from that originally employed.

Determination of Sulphuric Acid.—The filtrate and washings from the carbonate of baryta are carefully acidulated with hydrochloric acid, and the sulphuric acid precipitated as sulphate of baryta (p. 592).

SEPARATION OF POTASSA AND SODA.

ROCHELLE SALT (SEIGNETTE SALT). TARTRATE OF POTASSA AND SODA.



§ 408. The crystals should be dried, as usual, by pressure between blotting-paper.

About 20 grs. of the powdered salt are very gradually heated, and incinerated till perfectly white (p. 573). The residue is dissolved in water, the solution diluted considerably in a beaker, and acidulated with hydrochloric acid; the acid solution is heated in the beaker till all effervescence has ceased, when it is evaporated to a small bulk in a porcelain dish, then transferred to a weighed platinum capsule, evaporated to dryness (p. 573), ignited, and weighed.

The mixture of chloride of potassium and chloride of sodium which is thus obtained is dissolved in water, and the potassium determined as the double chloride of platinum and potassium, according to the directions given at p. 591. By calculating the amount of potassium thus obtained as chloride, and deducting the weight of the latter from that of the mixed chlorides, the weight of the chloride of sodium is ascertained. By a simple proportion, the weight of chloride of potassium or of sodium may be converted into that of the corresponding oxide (p. 591).

MARBLE.



§ 409. The best white marble should be taken. It is reduced to powder, and gently heated to expel adhering moisture.

Determination of lime; see p. 590.

Determination of carbonic acid; see p. 596.

SEPARATION OF LIME, MAGNESIA, AND SESQUIOXIDE OF IRON.

SEPARATION OF SILICIC ACID AND ALUMINA.

LIMESTONES.

§ 410. A specimen of limestone should be employed which has been previously analyzed qualitatively, and found to contain the following constituents: carbonates of lime and magnesia, oxide and sesquioxide of iron, oxide of manganese, clay (silicic acid and alumina), sand, water.

Determination of Water.—About 100 grains of the powdered limestone must be feebly ignited in a porcelain crucible (uncovered) for ten minutes; should the powder blacken during this ignition, it indicates the presence of organic matter, and the ignition must be continued till the dark color has disappeared. The crucible is then allowed to cool, and its contents wetted with a strong solution of carbonate of ammonia (to reconvert any caustic lime into carbonate); the crucible is then covered, and heated at a considerable distance above the flame, until it suffers no further alteration in weight; should the residue, when moistened with water, exhibit an alkaline reaction, the treatment with carbonate of ammonia must be repeated till no further alteration in weight is observed.

The loss of weight which the limestone has suffered in this process indicates the amount of water present; the determination, however, is not perfectly accurate, since the loss will be increased by the expulsion of the carbonic acid from the carbonates of iron and manganese, and by that of the organic matter; another source of inaccuracy is the conversion of the oxides of iron and manganese into higher oxides. However, the determination will be found sufficiently accurate for practical purposes.

Determination of Clay, Sand, Lime, Magnesia, and Iron.—About 100 grains of the powdered limestone are placed in a tall beaker covered with an inverted funnel to prevent loss from spirting, and about two ounces of water added; dilute hydrochloric acid is then added by small portions at a time, till all effervescence has ceased; the beaker is gently heated on a sand-bath, the residue allowed to subside, and collected on a filter of known ash; this residue is washed with hot water till the washings are no longer acid (these being mixed with the filtrate), dried, carefully incinerated, the ash moistened with nitric acid (to reoxidize any oxide of iron), dried, ignited, and weighed. After deducting the ash of the filter, we have the weight of the clay and sand contained in the limestone.

The proportions of these two ingredients may be judged of to some extent from the physical properties of the residue, since the sand would be gritty to the touch; or they may be roughly separated by suspension in water, when the particles of clay may be washed away, leaving the sand at the bottom. In order, however, to determine accurately the quantities of silica and alumina contained in this residue, from 10 to 20 grains of it, in a state of impalpable powder, should be mixed, in a platinum crucible, by means of a glass rod, with about 4 times its weight of carbonate of potassa and soda, and fused, by a gradually increasing heat, over a gauze burner or Argand spirit-lamp; after the mass has been retained in fusion for about half an hour, the crucible is allowed to cool, placed in a beaker (with inverted funnel), covered with water, and heated, with constant stirring, till the mass is, in great measure, disintegrated; hydrochloric acid is then added, by degrees, till it produces no more effervescence; the beaker is again placed on the sand-bath for some time, till no more bubbles of carbonic acid escape, the crucible removed (and well washed), and the contents of the beaker carefully evaporated to dryness in a porcelain dish; the residue is well dried, and mixed into a paste with concentrated hydrochloric acid—a little water added, the mixture heated for some minutes, more dilute hydrochloric acid added, the digestion continued for half an hour, and the solution filtered from the undissolved silica, which is well washed, dried, ignited, and weighed. The filtrate from the silica is mixed with excess of ammonia which throws down the alumina, to be washed, dried, ignited, and weighed.

The solution originally filtered from the clay and sand should be carefully measured or weighed.

About $\frac{1}{2}$ of this solution is mixed with a little concentrated nitric acid, and heated nearly to boiling (to peroxidize the iron); it is then allowed to cool, and mixed with excess of ammonia; the mixture is gently heated for a few minutes, and the precipitate collected, washed, dried, ignited, reoxidized with nitric acid, and weighed. Its weight represents that of the sesquioxide of iron (together with small quantities of silica, alumina, and sesquioxide of manganese, the two former of which render the precipitate of a lighter, and the latter, of a darker color than pure sesquioxide of iron) contained in the amount of limestone corresponding to the portion of solution employed.

The filtrate from the sesquioxide of iron is mixed with oxalate of ammonia as long as any precipitate is formed, the solution heated, the precipitated oxalate of lime treated as directed at p. 590; the filtrate and washings being set aside for the following determination. Since the lime is weighed in the form of car-

bonate, it is only necessary to calculate the percentage contained in the limestone.

In order to ascertain the amount of magnesia present, the solution filtered from the oxalate of lime is mixed with a considerable quantity of phosphate of soda, and the determination conducted as at p. 590. From the weight of the pyrophosphate of magnesia, the amount of carbonate of magnesia contained in the limestone may be readily calculated by the following proportion :—

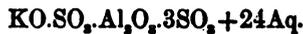
$$\begin{array}{l} 2MgO.PO_5, \quad 2(MgO.CO_2) \\ 112 \quad : \quad 84 \quad :: \text{Weight of ppt} : x, \end{array}$$

where x represents the weight of carbonate of magnesia to which the pyrophosphate corresponds.

The above method would, of course, serve, with some slight modifications, for the analysis of many calcareous minerals, and of specimens of clay, marl, &c.

SEPARATION OF ALUMINA AND POTASSA.

ALUM.



§ 411. The coarsely powdered crystals are dried between blotting-paper.

About 20 grs. of the salt are dissolved in water, and the *alumina* precipitated as directed at p. 585.

The filtrate and washings from the alumina are evaporated to a small bulk in a porcelain dish, afterwards transferred to a weighed platinum capsule, and the evaporation completed very cautiously in an air-bath (the capsule being covered with platinum-foil towards the conclusion). The dry residue is gradually ignited in the covered capsule, until no more fumes are perceived; the residual sulphate of potassa is allowed to cool, and weighed (p. 643). The sublimate of ammoniacal salts upon the cover is heated, and should any fixed residue remain, its weight must be determined and added to that of the sulphate of potassa in the dish.

The *sulphuric acid* is determined in 15 grs. of alum, as directed at p. 592.

SEPARATION OF THE OXIDES OF IRON AND CHROMIUM.

CHROME-IRON ORE.



§ 412. The mineral is powdered as finely as possible, about 15 grains of it intimately mixed with about the same quantity of carbonate of potassa and nitre, and fused for about an hour at a bright red heat, in a platinum crucible (which is not much attacked). The fused mass, together with the crucible, is placed in a beaker, and heated with water until completely disintegrated; the crucible is then removed (being well rinsed into the beaker), the solution filtered, and the residue well washed with hot water.

This residue, which contains generally some undecomposed mineral, together with sesquioxide of iron and some impurities of the ore, is treated with hot concentrated hydrochloric acid (for which purpose it is best to incinerate the filter), the undecomposed mineral filtered off, washed, ignited, and weighed,¹ and the iron precipitated from the solution by ammonia, being subsequently separated from any alumina which may be present, according to the method given in the analysis of clay (see 606).

¹ The weight of undecomposed mineral must, of course, be deducted from that originally employed.

The solution of chromate of potassa is treated, as at p. 595, for the determination of the chromium as sesquioxide.

Calvert has recently proposed the following as a more satisfactory method of analyzing chrome-iron ore.

About 15 grains of the finely powdered ore are intimately mixed with 3 or 4 parts of soda-lime (prepared by slaking quicklime with solution of caustic soda, drying and calcining) and about 1 part of nitrate of soda. The mixture is thoroughly ignited, in a platinum crucible, for 2 hours, being stirred frequently with a platinum wire. When cool, the mass is treated with water, to which a little dilute sulphuric acid is afterwards added; when the mass has been thus detached from the crucible, the latter is removed, and the solution mixed with alcohol, which precipitates the sulphate of lime, to be filtered off, and washed with dilute alcohol until the washings are colorless.

The residue on the filter may contain some undecomposed ore, mixed with the sulphate of lime; the latter may be removed by washing with boiling water, and the undecomposed ore subjected to a second oxidation.

The red solution containing the chromic acid is mixed with excess of ammonia and oxalate of ammonia, the precipitate (alumina, sesquioxide of iron, oxalate of lime, and silica) is filtered off, and well washed. The chromic acid may then be determined in the solution by reduction with alcohol and hydrochloric acid, and precipitation as sesquioxide of chromium (p. 595).

SEPARATION OF SILICA, ALUMINA, OXIDES OF IRON, LIME AND MAGNESIA. CLAY.

§ 413. Clay is composed chiefly of *silica, alumina, and water*; but generally contains, as impurities, *carbonates of lime, magnesia, oxide of manganese, oxide of iron, sand, and traces of alkalies.*

The amount of *water* in the original clay, which should first be dried as far as possible by exposure to air, may be determined as directed for limestones (p. 602).

For the subsequent analysis, the clay must be reduced to a very finely divided state.

About 20 grains of the finely powdered and ignited clay, are mixed and fused with carbonate of potassa and soda, as directed for quartz (p. 594); the fused mass is decomposed with dilute hydrochloric acid, and the *silica* determined exactly as in the case above referred to; the filtrate from the silica, which contains the bases, is concentrated by evaporation, a little nitric acid being added to peroxidize the iron.

The solution is then mixed with excess of ammonia (and, if much magnesia be present, some chloride of ammonium), gently heated, the precipitated *alumina, sesquioxide of iron*, and a little *sesquioxide of manganese*, filtered rapidly off, and well washed with hot water.

The *lime* and *magnesia* in the filtrate are determined as in the analysis of limestones.

The precipitate is dissolved in warm dilute hydrochloric acid, the filter being subsequently well washed. Should any residue of alumina remain undissolved, the filter may be dried, incinerated, and the weight of the alumina ascertained by deducting that of the ash.

The solution containing *alumina* and *iron* is introduced into a weighed dry flask, and its weight accurately determined.

About half of it is then poured into a beaker, and the weight of the flask again taken. The portion thus separated is precipitated with ammonia, the precipitate filtered off, washed, dried, ignited, and weighed, its weight being afterwards calculated for the whole quantity of the solution.

The other half is mixed with excess of solution of potassa (free from silica), heated for some minutes (in a silver vessel, or one of hard glass), and the precipitated *sesquioxide of iron* (with a little manganese) well washed with hot water, redissolved in hydrochloric acid, precipitated with ammonia, washed, dried, ignited, and weighed. If its weight be calculated for the whole quantity of solution, and deducted from that of the mixed alumina and iron, we obtain the amount of *alumina* present.¹

The amount of carbonic acid contained in the air-dried clay may be ascertained as directed at p. 596.

If the weight of the *sand* be required, it may be ascertained by boiling the clay with hydrochloric acid as long as anything is dissolved, washing the residue (silica and sand) with water, and boiling it repeatedly with a strong solution of carbonate of soda, which leaves only sand, to be washed, dried, ignited, and weighed.

SÉPARATION OF ALUMINA AND PHOSPHORIC ACID.

WAVELLITE.

§ 414. (*If this mineral be not procurable, artificial phosphate of alumina may be substituted for it.*)

Wavellite consists essentially of *phosphoric acid* and *alumina*, but generally contains, in addition, *oxide of iron*, *lime*, and *silica*.

It should be analyzed qualitatively, to ascertain its true composition.

The mineral is finely powdered, and dried by ignition.

About 20 grains of the finely powdered mineral are intimately mixed, in a platinum crucible, with about 80 grains of precipitated silica, and 120 grains of carbonate of soda. The mixture is cautiously fused for about an hour. When cool, the mass is digested with water, which dissolves the whole of the phosphoric acid and part of the silica, leaving the remainder of the latter, together with the alumina, iron, and lime, undissolved. Some carbonate of ammonia is added, and the solution digested for some time, at a gentle heat (in order to precipitate a little silica which has passed into solution).

The precipitate is filtered off, and well washed with hot water. The *phosphoric acid* is then determined in the solution, which must be previously acidified with acetic acid, as basic perphosphate of iron (*see* p. 593).

In order to determine the alumina, &c., the precipitate is dissolved off the filter with warm dilute hydrochloric acid, the solution evaporated to dryness, and the residue digested with hydrochloric acid; the solution is filtered from the undissolved silica, and the *alumina*, *sesquioxide of iron*, and *lime*, determined as in the analysis of clays (p. 605).

The *silica* contained in the mineral is determined as in quartz (p. 594).

ANALYSIS OF IRON ORES,

and determination of the relative quantities of oxides of iron.

§ 415. The iron may be very accurately determined in the wet way by the process of *Margueritte*, which depends upon the power possessed by the proto-salts of iron to reduce permanganic acid.

The process may be divided into three portions: 1. The preparation of a standard solution of permanganate of potassa; 2. The solution of the iron, and its reduction to the state of protoxide; and 3. The determination of the iron.

¹ Rivot introduces the ignited mixture of alumina and sesquioxide of iron into a small porcelain boat, and heats it to redness in a porcelain tube through which dry hydrogen is passed; when no more water is formed, showing that the reduction of the iron is complete, the mixture of alumina and metallic iron is digested with very dilute nitric acid, which dissolves only the latter, to be precipitated by ammonia, and determined.

In order to prepare the standard solution of permanganate of potassa, 2 parts of binoxide of manganese, 1 part of chlorate of potassa, and 3 parts of hydrate of potassa are fused in a Hessian crucible till the mass has a fine dark green color; it is then broken up, and digested with a moderate quantity of water; the solution is decanted from the residue, heated on a sand-bath, and nitric acid added, drop by drop, till the green solution of manganate of potassa is converted into the rose-violet of the permanganate; the solution is filtered through asbestos, and carefully preserved out of contact with organic matter.

To graduate this solution, about 15 grs. of piano-wire (accurately weighed) are dissolved in a moderate quantity of strong hydrochloric acid, and the solution divided (by measure) into two equal parts; one of these is introduced into a large flask, and diluted with about twenty ounces of water; the solution of permanganate is now added from a burette, very gradually, and with constant shaking, until a pale rose color pervades the liquid; the operation is repeated, even more carefully, with the second portion of the iron-solution, and the number of measures of permanganate which are necessary to oxidize 100 grs. of iron calculated from the mean of the two experiments.

It is advisable to have the solution of permanganate of such a strength that about 1000 grain measures correspond to 10 grs. of iron.

The action of a solution of permanganic acid upon (proto-) chloride of iron in presence of hydrochloric acid is represented in the following equation:—



We have now to obtain the iron in a state of solution, which is effected by boiling about 15 grs. of the finely powdered ore with hydrochloric or nitrohydrochloric acid, according to its nature; if the latter be employed, the solution must be evaporated with an excess of hydrochloric acid to expel the nitric acid, the residue being afterwards redissolved in hydrochloric acid. The solution is then boiled with a little concentrated solution of sulphite of soda until it has acquired a pale green color, and the smell of sulphurous acid has disappeared; in this way the whole of the sesquichloride of iron is reduced to (proto-) chloride.

If arsenic or copper be present in the ore, it is better to effect this reduction by boiling with a little zinc (free from iron), and to filter off the reduced metals.

The solution of iron is largely diluted with (about 30 ounces of) water in a spacious flask, and the permanganate-solution gradually added from the burette in the manner above described. Since we know the number of measures of the solution required to peroxidize 100 grs. of iron, we have only to calculate by a proportion the amount of metal present in the ore.

This method is very convenient, expeditious, and accurate, but unfortunately the solution of permanganate of potassa is gradually decomposed when kept, so that it is necessary to graduate the solution afresh before every series of determinations.

If it be desired to ascertain the *degree of oxidation* in which the iron exists in the ore, we may make one determination according to the above directions, and another in the hydrochloric solution of the ore, without adding any reducing agent. The first operation gives the total quantity of iron present, and the second, that which exists as (prot-) oxide; by difference, of course, we obtain the amount of sesquioxide.¹

¹ Penny has proposed a method for the determination of iron in ores, which consists in reducing the sesquioxide, as above, to the state of protoxide, and in adding to the diluted hydrochloric solution, a solution of a known weight of bichromate of potassa, from a burette, until a drop of the liquid no longer gives a blue or green color with a drop of

The determination of the *clay, sand, water, lime, and magnesia*, may be effected in the same way as in the analysis of limestones (*see p. 602*).

The *carbonic acid* is determined according to the directions given at p. 596.

SEPARATION OF THE OXIDES OF IRON AND MANGANESE.

MANGANIFEROUS SPATHIC IRON-ORE.

§ 416. The essential constituents of this ore are *carbonates of iron and manganese*, but it often contains *carbonates of lime, magnesia, &c.*

About 15 grains of the ore are dissolved in hydrochloric acid, the iron peroxidized with a little nitric acid, and the sesquioxide precipitated as succinate, according to the directions given at p. 586.

The *manganese* is precipitated from the filtrate as sulphide (*see p. 588*).

The iron may also be determined by means of a standard solution of permanganate of potassa.

The *carbonic acid* in spathic iron ores may be estimated as at p. 596.

CRYSTALLIZED SULPHATE OF COPPER.



§ 417. The powdered crystals are pressed between blotting-paper.

Determination of the Water of Crystallization.—About 20 grains of the salt, in fine powder, are dried in the water-oven till the weight ceases to vary.

Determination of the Water of Constitution.—The residue from the above experiment is dried on a sand-bath, at about 400° F. (204° C.), till its weight ceases to vary.

Determination of the oxide of copper, *see p. 579*.

Determination of the Sulphuric Acid.—About 20 grains of the salt are dissolved in water, and the solution precipitated by chloride of barium (*p. 592*).

SEPARATION OF CADMIUM AND ZINC.

CALAMINE.

§ 418. (*A specimen should be selected which contains both zinc and cadmium.*)

The mineral may be freed from extraneous moisture by drying in the water-bath.

A quantity of the mineral depending upon the amount of cadmium present, is dissolved in hydrochloric acid, and the *cadmium* precipitated from the highly dilute solution as sulphide (*see p. 581*).

The *zinc* is subsequently precipitated from the filtrate as carbonate (*see p. 589*).

SEPARATION OF IRON AND COPPER.

COPPER-PYRITES.



§ 419. 15 grains of the finely powdered mineral are treated with the most concentrated nitric acid, in a large, long-necked flask, and, when the oxidation is less violent, heat is applied until the *sulphur* separates in pure yellow globules, which are collected on a weighed filter, well washed, dried, and weighed.

solution of ferricyanide of potassium upon a white plate. The calculation is based upon the following equation:—



Since the solution of bichromate may be preserved for any length of time, this process would, in some cases, be preferable to that in which permanganate of potassa is used.

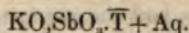
The solution is evaporated till the greater excess of nitric acid is expelled, largely diluted with water, and the sulphuric acid precipitated with chloride of barium. The amount of *sulphur*, calculated from the sulphate of baryta, is added to that obtained by direct weighing.

From the filtrate, the excess of baryta is removed by sulphuric acid (added in very slight excess) and the *copper* precipitated as sulphide (p. 579).

The solution filtered from the sulphide of copper is evaporated till all odor of sulphuretted hydrogen has disappeared, heated with nitric acid, to peroxidize the *iron*, which is then precipitated as sesquioxide, by ammonia (p. 586).

TARTAR EMETIC.

TARTRATE OF ANTIMONY AND POTASSA.



§ 420. About fifteen grains of the salt are dissolved in much water, the solution acidified with hydrochloric acid, and the *antimony* precipitated as tersulphide (p. 583).

The solution is evaporated, in the usual manner, to dryness, ignited till all organic matter is burnt off, and the *potassium* determined as chloride (p. 591).

SEPARATION OF TIN, ANTIMONY, COPPER, AND BISMUTH.

PEWTER.

§ 421. (*A good specimen should be employed, which has first been analyzed qualitatively, and found to contain the above metals.*)

Determination of Tin and Antimony jointly.—About 10 grains of the alloy, in small pieces, are oxidized with moderately strong nitric acid, in a beaker; most of the acid is evaporated off, the solution diluted with water, and the residue collected upon a filter, washed with hot water till the washings are no longer tinged by sulphuretted hydrogen, dried, ignited, with precautions, and weighed.

Determination of Antimony.—About 30 grains of the alloy are dissolved in hydrochloric acid, with addition of chlorate of potassa, and the antimony precipitated in the metallic state by means of a plate of tin (*see* p. 584.) The solution should first be heated gently, till it smells no longer of chlorous acid. If the metallic antimony be calculated as SbO_3 , and its percentage deducted from the percentage of residue left by nitric acid, it will furnish the amount of binoxide of tin, from which that of the tin may be calculated.

The following method has recently been proposed by Rose for the *separation of antimony and tin*.

The alloy is oxidized with nitric acid of sp. gr. 1.4. The excess of acid is expelled by evaporation, and the residual oxide heated to faint redness. It is then fused for some time in a silver crucible, with a considerable excess of pure hydrate of soda. The mass is dissolved in water, and so much alcohol, of sp. gr. 0.83, is added, that its volume may be to that of the water as 1 to 3. The mixture is allowed to stand for some time, in order that the whole of the antimoniate of soda may be deposited; it is then filtered off and washed, first with a mixture of equal volumes of water and alcohol of sp. gr. 0.83, and afterwards with a mixture of 3 volumes of alcohol of 0.83 and 1 volume of water, until a portion of the filtrate, after acidulation with sulphuric acid, is no longer precipitated, even after some time, by sulphuretted hydrogen. It is recommended to dissolve a little carbonate of soda in the weak spirit employed for washing.

The filtrate (containing the stannate of soda) is gently heated, to expel the alcohol, diluted with water, acidulated with sulphuric acid, and precipitated by

sulphuretted hydrogen. The bisulphide of tin is converted into binoxide by roasting, and weighed.

The filter containing the antimoniate of soda is placed, while yet moist, in a beaker, and treated with a mixture of hydrochloric and tartaric acids, the filter being afterwards washed with the mixture. The solution is saturated with sulphuretted hydrogen, the pentasulphide of antimony collected upon a weighed filter, washed, dried, weighed, and the antimony in it determined by reducing a weighed portion with hydrogen in a porcelain crucible, through the lid of which a small porcelain tube passes.

Should arsenic be present, it will be contained in the alkaline solution as arseniate of soda. This solution is acidulated with hydrochloric acid, any precipitate being disregarded and left in the liquid, and saturated with sulphuretted hydrogen. The solution is allowed to stand until the odor of sulphuretted hydrogen is scarcely perceptible, and the precipitate collected upon a weighed filter. The filtrate is heated with solution of sulphurous acid, and again saturated with sulphuretted hydrogen, when, if any sulphide of arsenic be precipitated, it may be collected upon a separate filter, since it contains no tin. The original precipitate, containing the two sulphides, is washed, dried, and weighed. A weighed portion of it is afterwards heated in a current of sulphuretted hydrogen, when the sulphide of arsenic is volatilized. The residual bisulphide of tin is converted into binoxide by roasting, and weighed; the sublimed sulphide of arsenic, together with the small portion upon the other filter, is converted into arsenic acid and determined (p. 584).

Determination of Copper and Bismuth.—About 30 or 40 grs. of pewter are oxidized with nitric acid, as for the determination of the tin and antimony, the solution filtered off, and the *teroxide of bismuth* precipitated by carbonate of ammonia, and determined as at p. 579.

The *copper* is precipitated from the solution by sulphuretted hydrogen, and the sulphide treated as directed at p. 579.

SEPARATION OF TIN, LEAD, AND BISMUTH.

ANALYSIS OF NEWTON'S FUSIBLE ALLOY.

§ 422. About 10 grs. of the alloy are oxidized with moderately dilute nitric acid, with the aid of heat, a considerable quantity of water is added, and heat again applied, in order that the nitrates of lead and bismuth may be completely dissolved; the solution is allowed to subside, the residue of *binoxide of tin* filtered off, and treated as directed at p. 582; the filtrate is evaporated to a small bulk, the *lead* precipitated as sulphate (p. 578), and the *bismuth* determined in the filtrate, as directed at p. 579.

SEPARATION OF ANTIMONY, LEAD, AND BISMUTH.

ANALYSIS OF TYPE-METAL.

§ 423. About 10 grs. of the alloy are completely oxidized with dilute nitric acid, the greater part of the excess of acid being expelled by evaporation; a considerable quantity of water is then added, and the whole boiled; the residue is collected on a filter, washed till the washings are no longer blackened by sulphuretted hydrogen, dried, incinerated with the usual precautions for easily reducible oxides, and weighed; the amount of *antimony* is then calculated from the weight of antimonious acid, as at p. 583.

The *lead* and *bismuth* may be determined in the filtrate in the same manner as in the analysis of Newton's fusible metal.

SEPARATION OF TIN, COPPER, LEAD, AND ZINC.

ANALYSIS OF BRASS, BRONZE, GUN-METAL, &c.

§ 424. These alloys are liable to contain, not only copper, zinc, and tin, but also small quantities of lead; the following method, therefore, will be applicable to specimens containing any of these metals.

About 10 grains of the alloy are boiled with moderately dilute nitric acid (1 volume of concent. acid and 3 volumes water) in a beaker covered with an inverted funnel, and the solution evaporated (in the same way) to a small bulk; a considerable quantity of water is then added, and the solution set aside till the residue has subsided; this residue consists of *binocide of tin*, the amount of which is determined as at p. 582.

The filtrate from the binocide of tin is mixed with a little pure dilute sulphuric acid, and evaporated to a small bulk to expel the greater part of the nitric acid; a little water is then added, and the precipitated *sulphate of lead* determined as at p. 578.

The filtrate from the sulphate of lead is diluted with a considerable quantity of water, and saturated with sulphuretted hydrogen; *the sulphide of copper* thus precipitated is treated as directed in p. 579.

The solution filtered from the sulphide of copper is evaporated considerably, to expel the hydrosulphuric acid, and to concentrate the solution, and the *zinc* afterwards determined as basic carbonate, according to the directions given at p. 588.

SEPARATION OF COPPER, ZINC, AND NICKEL.

ANALYSIS OF GERMAN SILVER.

§ 425. This alloy may be analyzed as follows:—

About 10 grains are dissolved in nitric acid, the solution evaporated till the greater excess of nitric acid is expelled, diluted largely with water, and a considerable quantity of hydrochloric acid added. The solution is then completely saturated with sulphuretted hydrogen, the precipitated sulphide of copper filtered off and treated as at p. 579. The filtrate and washings are evaporated to a small bulk, mixed with an excess of solution of acetate of potassa, and saturated with sulphuretted hydrogen; the precipitated sulphide of zinc is filtered off, and treated in the manner directed at p. 588. The nickel in the filtrate, which must be evaporated to expel excess of hydrosulphuric acid, is determined according to p. 587.

SEPARATION OF TIN, ANTIMONY, COPPER, AND LEAD.

BRITANNIA-METAL.

§ 426. The *tin* and *antimony* are determined as in the analysis of pewter (p. 609). The *lead* may be precipitated with carbonate of ammonia, and treated according to the directions given for oxalate of lead (p. 578); the *copper* is subsequently removed from the filtrate by sulphuretted hydrogen (p. 579).

SEPARATION OF SILVER AND COPPER.

ANALYSIS OF STANDARD SILVER.

§ 427. The analysis of alloys containing only silver and copper is very easily effected by dissolving them in nitric acid, precipitating the *silver* as chloride (p. 576), and subsequently precipitating the *copper* from the solution by potassa (p. 579).

The determination of silver in alloys may be effected with great rapidity and accuracy by using the standard solution of chloride of sodium, that is, a solution; a certain number of measures of which will precipitate, as chloride, a known quantity of silver.

The solution to be analyzed is mixed with some diluted nitric acid, gently heated, and the standard solution of chloride of sodium gradually added, with frequent agitation, until a drop fails to produce a fresh precipitate of chloride of silver; the number of measures of solution which have been used is then read off, and the quantity of silver calculated.

SEPARATION OF GOLD, SILVER, AND COPPER.

ANALYSIS OF STANDARD GOLD.

§ 428. The analysis of alloys of gold, silver, and copper, in the moist way, is attended with some difficulty.

The general method consists in laminating the alloy, and boiling with nitro-hydrochloric acid; if the metal becomes coated with chloride of silver, it must be carefully removed, and treated with ammonia, so as to expose a fresh metallic surface, the ammoniacal solution being afterwards neutralized with hydrochloric acid, and added to the solution in *aqua regia*; the residual *chloride of silver* is collected, and treated as at p. 576.

The solution containing the gold and copper is evaporated to dryness on a water-bath, the residue dissolved in hydrochloric acid, and again evaporated, to expel all nitric acid; it is then redissolved in dilute hydrochloric acid, and the solution boiled for some time with oxalic acid; the supernatant liquid is decanted from the precipitated *gold*, the latter washed with a little ammonia, to remove any oxalate of copper, then, with water, transferred to a weighed capsule, dried in an air-bath, ignited, and weighed.

The *copper* may be determined in the solution by precipitating with sulphuretted hydrogen, and subsequently converting the sulphide into oxide (p. 579).

AMALGAMS.

SEPARATION OF MERCURY AND ZINC.

§ 429. The amalgam used for electrical machines may be analyzed for practice.

Fifteen grains of the amalgam are dissolved in nitric acid, the solution evaporated with hydrochloric acid, on a water-bath, till all free nitric acid is expelled, and the *mercury* precipitated by sulphuretted hydrogen (p. 577).

The filtrate from the sulphide of mercury is evaporated to a small bulk, to expel excess of acid, and the *zinc* precipitated as basic carbonate (p. 588).

SEPARATION OF MERCURY AND TIN.

§ 430. Amalgam of tin may be analyzed by a process similar to the above, the *tin* being determined as binoxide (p. 582), and the *mercury* precipitated as sulphide (p. 577), or the mercury may be expelled by heat, and the tin converted into binoxide by roasting.

SEPARATION OF ARSENIC, COBALT, NICKEL, AND IRON.

SPEISS-COBALT.

§ 431. This substance contains *arsenic*, *cobalt*, *nickel*, *iron*, *sulphur*, and *silica*. Since the arsenic exists in very large proportion, it is well to determine it in a separate quantity.

Determination of Arsenic.—About 10 grs. of the finely powdered substance

are boiled in a large flask, with concentrated nitric acid, till no further action takes place. The solution is diluted with water, filtered, mixed with excess of ammonia and digested with colorless sulphide of ammonium, at a gentle heat, for a considerable time. The digestion should be conducted in a flask. The solution is filtered off, and the residue washed with water containing colorless sulphide of ammonium. (If yellow sulphide of ammonium were employed, some sulphide of nickel might be dissolved.) The filtrate is decomposed with a slight excess of acetic acid, and the precipitate of *pentasulphide of arsenic* treated as at p. 584.

If this precipitate should contain any sulphide of nickel or of copper, it may be dissolved in warm ammonia, and reprecipitated with acetic acid.

Another method of determining the arsenic consists in expelling the excess of acid from the nitric solution by evaporation; diluting largely with water, reducing the arsenic acid by sulphurous acid, evaporating the excess of the latter, and determining the arsenic as tersulphide (p. 584).

The treatment with sulphurous and hydrosulphuric acids must, however, be repeated several times, until no more arsenic is separated.

Determination of Sulphur.—About 20 grains of the substance are boiled with the strongest nitric acid, until the sulphur is either completely oxidized, or till the excess is separated in clear yellow globules; the solution is then diluted with water and passed through a weighed filter.

The sulphuric acid in the solution is determined as sulphate of baryta, from which the amount of sulphur is calculated.

The undissolved residue (sulphur and silica) is dried at 212° F. and weighed; it is then ignited in the usual manner, when the sulphur is volatilized and may be estimated from the loss.

Determination of Iron, Nickel, and Cobalt.—About 15 or 20 grs. of the ore are carefully roasted in a porcelain crucible, to expel as much as possible of the sulphur and arsenic. The roasted ore is then treated as before, with nitric acid, the solution evaporated to dryness, the residue digested with concentrated hydrochloric acid, water added, and the liquid filtered. The filtrate is saturated with sulphurous acid, digested for some time at a gentle heat, evaporated to expel excess of sulphurous acid, saturated with sulphuretted hydrogen, and allowed to stand for some time in a warm place; this treatment with sulphuretted hydrogen is repeated, until the odor no longer disappears after digestion for a short time. The precipitate is filtered off and washed. The filtrate is again treated, in the same way, with sulphurous and hydrosulphuric acids, as long as any arsenic is separated. The filtrate and washings are then concentrated by evaporation, and the iron separated as succinate (or benzoate) as directed p. 607.

For the separation of the *cobalt* and *nickel*, the solution (free from iron, arsenic, &c.), slightly acidified with hydrochloric acid, is mixed with a dilute solution of chloride of lime, to which a slight excess of sulphuric acid has been added, by which the chloride of cobalt is entirely converted into sesquichloride. A thin cream of pure carbonate of lime is then added in excess, and the mixture digested, in the cold, with frequent agitation, for at least 24 hours. The *nickel* remains in solution as chloride, while the cobalt is precipitated in the form of sesquioxide, mixed with the excess of carbonate of lime.

The precipitate is collected upon a filter and thoroughly washed; the filter is then placed in a capacious beaker, and covered with water, to which hydrosulphuric acid must be added from time to time, until the precipitate is entirely dissolved, which may be promoted by gently heating; the solution is separated from the filter-paper (which must be very thoroughly washed), concentrated by evaporation, mixed with ammonia in slight excess, and saturated with sulphuretted hydrogen; the precipitated *sulphide of cobalt* is filtered off and treated as at p. 587.

The solution containing the chloride of nickel is concentrated by evaporation, mixed with a slight excess of ammonia and saturated with sulphuretted hydrogen; the precipitated sulphide of nickel being dissolved in nitro-hydrochloric acid, and the *nickel* determined as at p. 587.

Another process for separating nickel and cobalt, known as *Liebig's method*, is executed as follows. The solution is mixed with a considerable quantity of hydrocyanic acid, and afterwards nearly neutralized with potassa; heat is then applied until the solution becomes clear and the excess of hydrocyanic acid is expelled. The cobalt is thus converted into cobalticyanide of potassium, and the nickel into the double cyanide of nickel and potassium. An excess of freshly precipitated well-washed oxide of mercury is now added to the hot solution, when the whole of the nickel is precipitated, partly as oxide, partly as cyanide. The solution is boiled for a short time, to convert the nickel entirely into oxide, which is collected upon a filter, washed, dried, and ignited, when the excess of oxide of mercury is expelled, and oxide of nickel alone remains.

The filtrate containing the cobalt is mixed with excess of acetic acid, and precipitated, while boiling, with sulphate of copper;¹ the mixture is boiled until the precipitated cobalticyanide of copper has become somewhat granular, and filtered. The precipitate is washed, dried, ignited, dissolved in hydrochloric acid with a little nitric, the solution largely diluted, and the copper precipitated by sulphuretted hydrogen; the solution filtered from the sulphide of copper is concentrated by evaporation, the cobalt precipitated as oxide, by boiling with potassa, and determined as usual.

DETERMINATION OF THE VALUE OF MANGANESE-ORES.

§ 432. Since the natural oxides of manganese are used chiefly for the preparation of chlorine in bleach-works, it is important that we should possess some ready method of ascertaining the quantity of chlorine which a given amount of the ore is capable of eliminating, as well as the quantity of hydrochloric acid consumed, which will depend upon the nature of the foreign matters contained in the ore.

In order to determine how much chlorine may be liberated by a certain amount of ore, about 100 grains of the latter, in a state of very fine powder, are heated with hydrochloric acid, in a flask provided with a bent tube, which conducts the chlorine into a weak solution of potassa contained in another flask; care is taken to evolve the whole of the chlorine, and the solution of hypochlorite of potassa and chloride of potassium is then tested by a chlorimetric process (p. 615).

To ascertain how much hydrochloric acid is consumed in the evolution of the chlorine, about 50 grains of the finely powdered ore are dissolved at a gentle heat in a measured quantity of dilute acid (of known strength), and the excess of acid remaining is then determined, after the complete expulsion of the chlorine, by adding a standard solution of carbonate of soda until a permanent precipitate begins to be formed.

A very neat method of testing the ores of manganese is that of Fresenius and Will, which consists in treating the ore (previously freed from earthy carbonates by washing with dilute nitric acid) with oxalate of potassa and sulphuric acid, when the oxalic acid (C_2O_3) is converted into 2 eqs. of carbonic acid, the weight of which is ascertained from the loss suffered by the apparatus (so constructed that no aqueous vapor shall be carried off).

¹ Wöhler recommends the precipitation of the solution, nearly neutralized with nitric acid, by a solution of nitrate of suboxide of mercury, which precipitates the mercury as cobalticyanide; the latter, when washed, dried, and ignited, leaves the black intermediate oxide of cobalt.

the quantity of available chlorine present in the bleaching-powder is calculated according to the equation



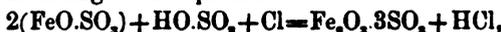
by which it will be seen that 99 parts, or one equivalent, of arsenious acid correspond to 71 parts, or two equivalents, of available chlorine.¹

$$99 : 71 :: \text{Arsenious acid employed} : x \\ x = \text{Available chlorine.}$$

The method most commonly used, however, for determining the value of specimens of bleaching-powder, is to ascertain the quantity of the latter which is required to peroxidize a known weight of the green sulphate of iron.

Pure crystals of the sulphate are powdered and dried, by pressure between folds of blotting paper; about 50 grains of the powder are accurately weighed, and dissolved in about 1000 grain-measures of cold water; the solution is then acidified with sulphuric acid.

The solution of bleaching-powder, prepared as in the last method, is then poured from a burette into the liquid, until the latter ceases to give a blue precipitate in a drop of solution of ferricyanide of potassium (placed on a white plate), showing that all the oxide of iron has been converted into sesquioxide. The amount of bleaching-powder employed is then calculated, and the available chlorine deduced according to the equation



by which we see that 278 parts, or 2 eqs., of crystallized sulphate of iron ($\text{FeO} \cdot \text{SO}_3 \cdot \text{HO} + 6\text{Aq}$) correspond to 35.5 parts, or 1 eq., of chlorine.²

$$278 : 35.5 :: \text{Sulphate of iron employed} : x \\ x = \text{Available chlorine.}$$

ALKALIMETRY.

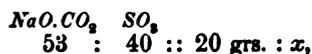
Fig. 78. § 484. The methods of determining the amount of available alkali contained in various specimens of commercial potash and soda are known by the name of alkalimetry. We shall first consider the valuation of potash, and subsequently the modifications necessary in the case of soda.



The older alkalimetric process consists in ascertaining how many measures of dilute sulphuric acid of known strength are required to neutralize a given quantity of carbonate of potassa. For this purpose a test-acid is first prepared by mixing about 1000 grs. of pure oil of vitriol with about 10,000 grs. of water; this acid is graduated in the following manner; about 20 grs. of perfectly pure and dry carbonate of soda are accurately weighed and dissolved in water; the solution is colored blue with a few drops of tincture of litmus, and the test-acid slowly added from a graduated burette, the liquid being constantly stirred. The first addition of acid merely converts the carbonate of soda into bicarbonate; carbonic acid is afterwards liberated, and colors the litmus wine-red, but when an excess of acid is added, a bright red tint is produced, which indicates that the operation is completed. Having now observed the number of measures of dilute acid employed, we have only to calculate the amount of real acid which they contain.

¹ Penot has modified this process. He dissolves 4.44 parts of arsenious acid, and 13 parts of crystallized carbonate of soda in water, and adds this solution, from a burette, to the solution of a known weight of chloride of lime, until the liquid no longer produces a blue color upon a test-paper impregnated with 1 part of iodine, 7 parts of crystallized carbonate of soda, and 3 parts of starch, heated with water until the blue color has disappeared.

² Müller has proposed a new method for the valuation of chloride of lime. A standard



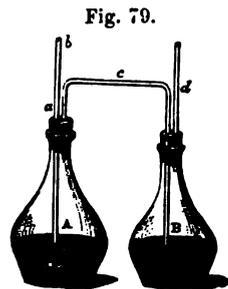
where x represents the *weight of* SO_2 contained in the number of measures of test-acid employed. In making use of this acid in alkalimetric determinations, it will only be necessary to remember that 1 eq. or 40 parts by weight of SO_2 , correspond to 1 eq. or 47 parts by weight of available potassa, or 31 parts by weight of available soda.

In order to test the carbonate, a fair sample (about 30 grs.) is dissolved in water, filtered, if necessary, taking care to wash the filter, and the solution treated in exactly the same manner as above described for the solution of carbonate of soda; the amount of available potassa present may then be calculated from the number of measures of acid employed.

This process is very simple, but liable to inaccuracy from various sources; thus, the sulphide of potassium which is generally contained in crude potashes neutralizes a certain quantity of acid, thus indicating too large an amount of alkali. Moreover, the presence of carbonate of soda in the specimen examined would give rise to error.

The alkalimetric method of Fresenius and Will is far more accurate than the above, though less easy of execution. It consists in decomposing the alkaline carbonate by means of sulphuric acid in an apparatus so constructed that the carbonic acid evolved passes through oil of vitriol, and therefore carries off no moisture with it, so that the loss of weight of the apparatus after the operation represents the amount of carbonic acid which was present in the carbonate examined. If any sulphide of potassium be present in the specimen, a little chromate of potassa is added, to oxidize the sulphuretted hydrogen which is liberated; of course, the presence of carbonate of soda would also give rise to error in this process, but, in such a case, a combination of the two alkalimetric methods would be advantageous.

The apparatus employed in this process consists of two flasks (Fig. 78), the *generator* A, which should be capable of containing about three fluidounces, and the *drying-flask* B, of about two ounces capacity; their necks should not be very wide. The generating-flask is fitted with a very sound cork, *a*, furnished with two rather narrow tubes, one of which, *b*, is straight, and passes nearly to the bottom of the flask, while the other, *c*, is bent twice at right angles, so as to form two limbs of unequal length, the shorter of which merely passes through the cork of the generator, while the longer reaches down to the bottom of the *drying-flask*; through the cork of the latter, another straight tube, *d*, is inserted, which must only project a little into the flask. The horizontal portion of the tube between the two limbs should be of such a length that the flasks which it connects may almost touch each other.



In order to determine the value of a specimen of alkali with this apparatus, an accurately weighed quantity (20 or 30 grs.) is shaken out of the weighing-bottle into the generating-flask, where it is covered with about half an inch of water; the generator is then connected with the drying-flask, which is about

solution of protochloride of tin is graduated by ascertaining how many measures are required to decolorize a solution of sesquichloride of iron, of known strength, to which a little sulphocyanide of potassium has been added. A measured quantity of the tin-solution is treated with the solution of a given amount of chloride of lime, and the amount of tin remaining unconverted into bichloride is then determined by means of the above iron-solution. Since the tin corresponds, equivalent for equivalent, to the available chlorine, the calculation is very simple.

three parts filled with concentrated sulphuric acid. In order to ascertain whether the apparatus is perfectly air-tight, the straight tube *a* of the generating-flask is closed with a little plug of wax, and a few bubbles of air are sucked out of the apparatus through a piece of caoutchouc tube fitted on to the straight tube *d* of the washing flask. If, when the suction is discontinued, the sulphuric acid rises in the longer limb of the bent tube, and retains its level for a minute or two, the apparatus is tight, but should it fall gradually, the corks must be carefully inserted a little further into the necks, and, if this fail, they must be replaced by fresh corks. When the operator is assured of the efficiency of the apparatus, the caoutchouc tube is removed, and the weight of the whole arrangement carefully determined. The caoutchouc tube is then replaced, and suction applied as before, so as to rarefy the air in the generator, thus allowing the pressure of the external air to force a small quantity of sulphuric acid over when the suction is discontinued; care must be taken not to force over too much acid at first; the contact of the sulphuric acid with the solution of the carbonate in the generator gives rise to a sudden evolution of carbonic acid, the greater part of which is absorbed by the undecomposed carbonate, which it converts into bicarbonate; when the action appears to have ceased, a fresh portion of the acid is drawn over, and this is repeated at intervals as long as it produces effervescence, the quantity of acid being regulated according to the passage of the bubbles through the sulphuric acid. At the end of the operation, a considerable quantity of acid is forced over, so as to heat the contents of the generating-flask considerably, in order that the last traces of carbonic acid may be expelled; the wax-stopper is then removed from the straight tube of the generator (and placed upon the cork of the latter, so that it may be weighed, as before, with the apparatus), and air slowly sucked through the drying-flask (for about five minutes) as long as it tastes of carbonic acid. It will be obvious, that, at the commencement of the operation, so much acid should be placed in the drying-flask that enough may be now left to effect the exsiccation of the gas which passes through it; this requires especial attention, on account of the higher temperature of the generating-flask, which promotes the vaporization of the water.

The apparatus is now allowed to cool, and weighed. The difference between the two weighings gives the amount of carbonic acid.

Calculation.

$$\begin{array}{l} CO_2 \quad KO.CO_2 \quad NaO.CO_2 \\ 22 \quad : \quad 69 \quad \text{or} \quad 53 \quad :: \quad \text{Loss of weight} : x \\ x = \text{Weight of carbonate of potassa or of soda.} \end{array}$$

The amount of available alkali contained in any specimen of the carbonate of soda may be ascertained by the methods just described; should the specimen to be examined contain any hydrate of soda, its amount may be ascertained by making two determinations of carbonic acid, according to the method of Fresenius and Will, one determination being made with the original alkali, the other with a weighed portion which has been moistened with carbonate of ammonia and ignited, in order to convert the hydrate of soda into carbonate; of course, the increase of carbonic acid in the last experiment will correspond to the amount of hydrate of soda present.

If the soda to be examined contain much carbonate of lime, it is necessary to separate it before estimating the carbonic acid; this may be effected by exhausting a known weight of the specimen with water, filtering from the carbonate of lime, taking care to wash the filter, and evaporating the filtrate and washings to dryness; the dry residue may be employed for the determination of carbonic acid.

The presence of sulphide of sodium and hyposulphide of soda in a specimen of the carbonate may be ascertained by dissolving in water, rendering the solution slightly yellow with a few drops of bichromate of potassa, adding excess of hy-

droehloric acid, and gently heating; if either of these salts be present, the solution will assume a green color; in the process of Fresenius and Will, it is recommended, if the alkali contain much sulphide of sodium or hyposulphite of soda, to introduce a little chromate of potassa into the flask from which the carbonic acid is evolved, in order to oxidize these salts, and convert them into sulphate of soda. If much chloride of sodium be present, the excess of chromic acid will give rise to a disengagement of chlorine from this salt; this chlorine, being evolved as gas, will, of course, add to the loss of weight of the apparatus, and thus increase the apparent amount of carbonic acid. In order to avoid this, the aqueous solution of a weighed quantity of the carbonate may be mixed with a little chlorate of potassa, evaporated to dryness in a platinum dish, and gently ignited; in this way, the sulphide of sodium and hyposulphite of soda will be converted into sulphates, and the carbonic acid may now be determined in the residue without the use of chromate of potassa.

ACIDIMETRY.

Determination of the strength of a specimen of Dilute Nitric Acid (HONO₂).

§ 435. A weighed or measured portion of the acid is tinged with litmus, and cautiously neutralized with a solution of carbonate of soda of known strength (see Alkalimetry, § 434), added from a burette, until the clear red color gives place to the wine-red tint caused by free carbonic acid. The amount of real acid is then inferred from the quantity of carbonate of soda employed.

2. A more accurate method consists in placing a certain quantity of the acid in the generating-flask of a Fresenius and Will's apparatus, and suspending, by means of a horsehair, a small bottle containing more bicarbonate of soda¹ than is sufficient to neutralize the acid employed. When the apparatus is arranged and weighed, as usual, the acid is gradually rinsed into the bicarbonate, until no more carbonic acid is evolved, when the generating-flask is heated to about 130° F., air drawn through in the usual manner, as long as it tastes of carbonic acid, the apparatus allowed to cool, and weighed.

Every two equivalents of carbonic acid evolved correspond to one equivalent of real acid in the sample analyzed.

This method is applicable to the determination of the strength of other dilute acids.

ANALYSIS OF GUNPOWDER.

§ 436. I. *Determination of Moisture.*—About 20 grains of the powder, very finely pulverized, are exposed over sulphuric acid, *in vacuo*, until a constant weight is obtained.

For ordinary purposes, the moisture may be determined by exposing the powder to the temperature of the water-oven, until it ceases to lose weight. A slight excess is generally obtained by this method, since a small portion of the sulphur in the powder is expelled, together with the moisture.

II. *Determination of Nitre.*—The dried powder is transferred to a small beaker, in which it is drenched with about three ounces of hot water, and allowed to digest for some time upon a sand-bath at a moderate heat. It is then thrown upon a filter of known weight, previously moistened, and is washed with hot water, until a drop of the filtrate, which must be carefully collected, leaves no residue when evaporated upon platinum foil. The filter and residue are then dried in the water-oven (or, still better, *in vacuo*), until their weight is constant. The difference in weight between the residue (*minus* the weight of the filter) and the powder employed, will represent the amount of nitre.

¹ This must be perfectly free from carbonate.

To control this result, the filtrate and washings, obtained as above directed, are carefully concentrated in a porcelain-dish, at a moderate heat, upon a sand or air-bath, and afterwards transferred to a weighed platinum (or porcelain) capsule, and evaporated to dryness on a water-bath; the residue is then exposed to a temperature of 300° F. (149° C.), in an air-bath, until it ceases to lose weight. The quantity of nitre is thus determined directly.

III. *Determination of Sulphur.*—This ingredient may either be determined directly, or by the loss of weight sustained by dry powder, upon its removal.

Direct Determination.—1. About 20 grains of the dried powder are mixed with an equal weight of pure carbonate of soda (or of potassa), about 20 grains of nitre, and 80 grains of pure chloride of sodium are then added, the whole intimately mixed, and then submitted to fusion in a platinum crucible, the operation being conducted, and the sulphuric acid determined in the fused mass, in the manner directed at p. 599.

2. A tube of hard glass, provided with two bulbs, is accurately weighed; about 20 grains of dried powder are introduced into one of the bulbs, and the weight of the tube and powder noted (the difference between the two weights will represent the amount of powder employed). The extremity of the tube nearest to the bulb containing the powder is then attached to an apparatus in which dry hydrogen is disengaged. A slow current of gas is allowed to pass through the tube; as soon as the atmospheric air is completely expelled, the bulb containing the powder is moderately heated by means of a spirit-lamp, when the sulphur will vaporize, and pass over into the second bulb, where it will again condense; the space of tube between the two bulbs must be warmed with the spirit-lamp from time to time, to prevent any sulphur from condensing there. When no more sulphur is expelled from the powder, which is finally exposed to a temperature approaching dull redness, the tube is allowed to become nearly cool; it is then carefully cut with a very sharp file between the two bulbs, and each part is afterwards weighed, cleaned out, and reweighed. The amount of sulphur found in the second bulb should correspond, within the limits of error (0.5 per cent. loss), to the difference between the first and the final weight of the powder.

A slight loss of sulphur by this method is unavoidable, small portions being carried off mechanically by the current of hydrogen, if ever so slow, while a small quantity is also converted into hydrosulphuric acid.

By adopting the following modification of this method, very accurate results may, however, be arrived at:—

Instead of a tube with two bulbs, one of rather wider bore, about 8 inches in length, is employed, provided with only one bulb, at about 2 inches from one extremity of the tube. A small plug of dry asbestos having been introduced into the long arm of the tube, about $\frac{1}{2}$ inch distant from the bulb, the former is filled with thin filaments of dry bright copper, or of the finely divided metal, reduced from the oxide by hydrogen. The tube is then accurately weighed, the dried powder (from which the nitre has been removed) introduced into the bulb, and the weight again ascertained (the difference will give the amount of powder employed). The operation is then conducted as before, with this difference, that the copper is first raised to a red heat, and maintained at that temperature, before the sulphur is expelled from the powder. The sulphur-vapor, coming in contact with the heated metal, will at once combine with it, and no loss whatever is sustained. When the operation is completed, and the tube is cooled down sufficiently to be handled without inconvenience, it is carefully cut between the asbestos-plug and the bulb; the latter, containing the charcoal, is then placed on the balance while warm, and rapidly weighed; the loss of weight expresses the amount of sulphur, which may also be directly inferred from the increase of weight of the tube containing the copper.

Indirect Determination.—A weighed portion of the dry residue of carbon and sulphur left on extracting the powder with water, is introduced into a small

flask, and boiled for some time with a solution of sulphide of potassium or of sodium, or of sulphite of potassa or soda, until the whole of the sulphur is removed. The carbon is then collected upon a weighed filter, well washed, dried in a water-oven, and weighed; the difference between this weight and that of the original residue of carbon and sulphur indicates the amount of the latter, which must now be calculated for so much of this residue as would be furnished by 100 parts of gunpowder; the result is the percentage of sulphur.

The alkaline sulphides or sulphites employed to dissolve the sulphur must be perfectly free from caustic alkali, since the latter is capable of attacking charcoal which has not been very thoroughly charred. A mixture of bisulphide of carbon and alcohol may also be employed to extract the sulphur.

The results obtained by the indirect method are invariably too low, since the extraction of the sulphur is never complete.

IV. *Determination of Carbon.*—The amount of this constituent will have been ascertained by difference, and controlled by direct weighing in the preceding determinations. It is sometimes necessary, especially when *charbon roux* has been employed, to determine the amount of hydrogen contained in the charcoal; this is effected by burning a weighed quantity with oxide of copper in the manner to be described in a future part of the work, under the head of Organic Analysis.

ANALYSIS OF INSOLUBLE SILICATES.

ANALYSIS OF GLASS.

§ 437. It is of the highest importance that the glass to be examined should be first reduced to the most minute state of division; this is effected by levigation, in the manner described at p. 86.

The general method to be pursued in the analysis of glass containing lead differs necessarily somewhat from that employed in the analysis of all other kinds of glass. By the following methods, all ordinary constituents of glass may be determined; if the specimen to be examined contain any of the more rarely occurring bases, these may be readily determined, according to the appropriate methods.

Analysis of Glass containing no Lead.—From 20 to 30 grains of the finely-powdered glass, which has been first thoroughly dried, are mixed in a platinum crucible of sufficient capacity, with from 3.5 to 4 times that weight of pure, dried, and finely-powdered carbonate of soda. The mixture may be effected by stirring with a small glass rod, rounded at the extremity; this stirring must be continued until the mixture appears perfectly uniform; any particles adhering to the rod may afterwards be carefully removed into the crucible by means of a pigeon's feather. The crucible, having been carefully closed, is placed in a moderate sized Hessian crucible, into which has been tightly pressed a quantity of calcined magnesia sufficient to fill it to about one-half; the platinum crucible is carefully pressed into this bed of magnesia to such an extent as to be firmly supported thereby on all sides; it is thus maintained in a secure position during its subsequent exposure to a furnace-heat, and is prevented from coming in contact with the Hessian crucible, to the bottom or sides of which it might otherwise become attached during the operation. The Hessian crucible is now closed with a good cover, and placed upon a brick support in an ordinary furnace,¹

¹ This fusion may be more conveniently effected over a good gas-burner, especially if a mixture of pure carbonate of potassa and soda be employed, and the crucible placed in a jacket. In order to avoid violent effervescence, the mixture should be *fritted* by a gentle heat for half an hour, so that most of the carbonic acid shall be expelled before the heat is so far increased as to fuse the mass.

containing only a small fire; the crucible is carefully surrounded with coke, and the temperature then gradually raised, until the crucible has attained a bright red heat, in which state it is maintained for nearly an hour; it is then allowed to cool gradually. When the temperature is sufficiently low, the platinum crucible is removed and opened¹ (any adhering particles of magnesia having been first carefully removed from the exterior). It is generally found that portions of the mass have been thrown upon the inner surface of the cover, by the effervescence occasioned by the escape of carbonic acid during the fusion; both the crucible with its contents and the cover, are therefore introduced into a moderate-sized beaker, which is then filled about one-third with water, strongly acidulated with pure hydrochloric acid; the mouth of the beaker is closed with a light inverted funnel, immediately upon the introduction of the liquid, to prevent any loss from the effervescence that ensues as the fused mass comes in contact with the acid; the beaker is then maintained at a gentle heat, until the contents of the crucible are completely detached. When the glass under examination contains much manganese, water alone must be used for extracting the fused mass from the crucible, since hydrochloric acid would be decomposed by the manganic acid formed in the fusion, chlorine being evolved, which would act injuriously on the platinum crucible. In such cases, after the fused mass has been perfectly removed from the crucible, an excess of hydrochloric acid is very gradually added to the aqueous solution. An acid solution of the mass having been obtained² (the crucible and lid being carefully removed from the beaker and washed, over the latter, with a little distilled water), it is carefully transferred to a porcelain dish, and evaporated to dryness, in an air-bath, at a moderate temperature.

The residue obtained by this evaporation is moistened, when cool, with concentrated hydrochloric acid, and allowed to digest for some time. Water is then added, and the insoluble residue, which consists of the whole of the silicic acid, collected upon a filter, thoroughly washed (the filtrate and washings being preserved), dried, ignited according to the usual method, and weighed. Since ignited silica is very apt to be carried away by the stream of gas evolved during the incineration of the filter, it is advisable to transfer as much of the silica as possible to a weighed porcelain crucible, in which it is ignited, apart from the filter, which is subsequently incinerated in a platinum crucible, the ash being afterwards added to the silica.

In the hydrochloric acid solution, together with the washings, obtained as above, the various bases existing in combination with the silicic acid in the glass, with the exception of the alkalis, are determined.

This solution is heated with a little nitric acid, to peroxidize any iron; it is then mixed with a considerable quantity of solution of chloride of ammonium, to retain the magnesia in solution (and also the protoxide of manganese, if there be any), and afterwards with ammonia in excess, which precipitates the *sesquioxide of iron* and *alumina* together; this precipitate is washed, dried, ignited, and weighed; it is afterwards dissolved in hydrochloric acid; this solution is then digested at a gentle heat with a considerable excess of pure potassa, which retains the alumina in solution, while the sesquioxide of iron is precipitated. This precipitate frequently retains a small portion of the alumina, and also of the potassa

¹ If the glass contained manganese, the fused mass obtained as above will possess a bluish green or greenish color, according to the quantity present.

² A quantity of the silicic acid, in the gelatinous state, is generally suspended in the solution, a portion only being dissolved in the acid, unless a very large excess of alkaline carbonate was employed in the fusion. To ascertain whether the glass has been perfectly decomposed by the fusion, the liquid is stirred with a glass rod, which is allowed to rub against the sides and bottom of the beaker; any undecomposed glass would be immediately indicated by a grating noise.

that has been used as precipitant; it is therefore collected, and again dissolved in hydrochloric acid, and reprecipitated by excess of potassa,¹ filtered off (the filtrate, &c. being added to the other potassa-solution), and, after being thoroughly washed, dried, and weighed as sesquioxide of iron (p. 586). The difference between the weight of this sesquioxide and that of the first precipitate, would give the amount of alumina present in the glass, which may also be directly determined in the potassa-solution from which the iron was separated (provided the potassa employed was free from alumina) by acidifying with hydrochloric acid, and precipitating the hydrate of alumina by excess of ammonia (p. 587).

In the solution from which the alumina and sesquioxide of iron have been separated, the *lime* and *magnesia* are determined in the manner described in the analysis of limestones (p. 603).

The *alkalies* present in the glass must, of course, be determined in a fresh portion; the following is the most approved method:—

A flat-bottomed, cylindrical box, about six inches in diameter, and four inches high, is provided with a tightly-fitting leaden cover. The bottom of the box is then covered with a layer of about half an inch of powdered fluor-spar, which should be free from silica and galena, and to this is added sufficient concentrated sulphuric acid to form a thick paste. A weighed portion, about 30 grains, of the finely-powdered glass, is placed in a platinum dish, and covered with strong solution of ammonia. This dish having been placed in the centre of the box, supported upon a leaden ring of about 1½ inch in height, so as not to come in contact with the fluor-spar, the cover is adjusted, and the box placed on a sand-bath, where it is maintained for some time at a gentle heat.

The sulphuric acid soon acts upon the fluoride of calcium (fluor-spar), giving rise to the evolution of hydrofluoric acid, which is immediately absorbed by the ammonia with which the powdered glass is covered. The resulting fluoride of ammonium acts rapidly on the silicic acid of the glass, terfluoride of silicon and water being produced, and the bases thus gradually liberated from their combinations with silicic acid.

After having been subjected to the action of the hydrofluoric acid for about 10 or 12 hours, the dish should be placed in an air-bath, its contents completely dried, gently ignited, until no more fumes are evolved, and weighed. The contents of the dish are then again moistened with ammonia, and the whole operation repeated, until an hour's exposure to the action of the hydrofluoric acid produces no alteration in the weight of the dry mass.

After the complete decomposition, the dry residue, containing the metals in the form of fluorides, is digested at a gentle heat with concentrated hydrochloric acid, a little water being subsequently added, until the whole is dissolved. The solution is then evaporated to dryness, the residue redissolved in a little water, and heated with hydrate of baryta, which must be perfectly free from alkalies, until it has a distinct alkaline reaction. The liquid is then filtered from the precipitate (sesquioxide of iron, alumina, magnesia), the latter washed with about half a pint of hot water, which is afterwards mixed with the filtrate. The whole solution is mixed with a little free ammonia, and carbonate of ammonia added sufficient to precipitate the whole of the alkaline earths (baryta and lime), which may be aided by a gentle heat. The precipitated carbonates having been filtered off and washed, the solution is evaporated on a sand-bath to a small bulk, when it is transferred to a weighed platinum or porcelain dish, evaporated to dryness in an air-bath, and afterwards very gradually ignited, until no more fumes are evolved. It is advisable to cover the dish with a piece of platinum

¹ When the quantity of sesquioxide of iron present is considerable, and that of alumina comparatively small, it is necessary to repeat this operation three or four times, in order to insure the perfect separation of these two substances.

foil, in order to avoid loss by spirting. The alkaline chlorides should be rapidly weighed, whilst still rather warm, to prevent absorption of moisture.

The amounts of potassa and soda in these chlorides are determined as in Rochelle salt (p. 602).

The older method for the determination of alkalies, which is still employed by some chemists, is as follows:—

About 20 grains of the finely powdered glass are intimately mixed with from 8 to 4 parts of dry hydrate of baryta (which has been carefully tested for alkalies), and pretty strongly ignited in a platinum crucible,¹ for about an hour, over a good gas-burner. The agglutinated mass is then detached from the crucible, by gently squeezing the latter, and treated in a beaker, with dilute hydrochloric acid, in the manner described at p. 622. If necessary, the crucible and its cover may also be immersed in the acid. The solution is carefully evaporated to dryness in an air-bath, the residue digested with a little water, and hydrate of baryta added, till the reaction is distinctly alkaline. The precipitate is removed by filtration, and repeatedly washed with hot water, which is allowed to mix with the filtrate. The latter is then treated with ammonia and carbonate of ammonia, and the subsequent processes conducted as described above.

Analysis of Glass containing Lead.—The silicic acid cannot be determined in glasses of this class by fusion with alkaline carbonates, as just now described, since the presence of lead forbids the use of platinum crucibles, whilst porcelain crucibles cannot be employed, as the alkaline carbonate would attack them, taking up from their surface a portion of silica.

The following method, in which the silicic acid is determined indirectly, appears to yield correct results.

About 30 grains of the finely powdered glass are decomposed by fluoride of ammonium in the manner described above; the resulting mass is evaporated to dryness, and the residue digested with pure concentrated nitric acid at a gentle heat, whereby the various bases are converted into nitrates. Water is afterwards added, and the liquid evaporated to dryness in an air-bath. The residue is dissolved in much water, with two or three drops of dilute nitric acid, and the solution completely saturated with sulphuretted hydrogen. The precipitated sulphide of lead is collected upon a filter of known ash, washed and set aside to dry, the solution is evaporated to expel excess of sulphuretted hydrogen, and subsequently treated in the manner already described, p. 622, for the determination of iron, alumina, lime, and magnesia. The dried sulphide of lead is transferred from the filter to a weighed porcelain crucible, the filter is then held over the crucible with a pair of forceps, kindled and allowed to smoulder until entirely consumed, the ash being allowed to fall into the crucible. The contents of the latter are then moistened with concentrated nitric acid, very carefully dried in an air-bath, afterwards ignited, and weighed.

The alkalies are determined in a separate portion of glass, as directed p. 623.

The difference between the original weight of the glass and joint weight of the various oxides obtained by analysis, would give the amount of silicic acid present, though somewhat augmented by the loss which is inevitable in the determination of the other constituents.

CAST-IRON.

§ 438. A piece of gray cast-iron should be taken; it may be reduced to a fine state of division with the aid of a very sharp file.

The only constituents which it is generally necessary to determine in cast-iron,

¹ As long as the temperature is kept within moderate limits, the platinum crucible is not attacked by the baryta; the use of a silver crucible is attended with danger, on account of the comparatively easy fusibility of the metal.

are iron, carbon (combined and uncombined), sulphur, phosphorus, silicon, manganese, calcium, and sodium.¹

Determination of the total amount of Carbon.—About 50 grains of the fine iron filings are mixed with about 20 times as much chromate of lead, in a shallow porcelain mortar; $\frac{1}{4}$ of the mixture is set aside, and the remaining $\frac{3}{4}$ are intimately mixed with about 50 or 60 grains of chlorate of potassa.

This mixture is then introduced into a combustion-tube of hard glass, similar to those employed in organic analysis. It is well to introduce first an inch or two of a pure mixture of chlorate of potassa and chromate of lead. The remainder of the mixture is then also introduced into the tube, and the whole shaken down so as to allow a free passage for the gas evolved. The tube is placed in a Liebig's combustion-furnace, and connected, by a very sound cork, with a chloride of calcium tube, to absorb any water which may be evolved. To the chloride of calcium tube is attached, by means of a caoutchouc connector, a Liebig's potassa-apparatus, containing a solution of potassa of sp. gr. 1.27. The weight of this apparatus must be most accurately determined at the commencement of the experiment.

In order to ascertain whether the apparatus is tight, a few bubbles of air are cautiously sucked out through the potassa-apparatus, which is inclined for that purpose, so that the orifice of the egress-tube may be from potassa (as it should be throughout the experiment). If, after a few bubbles of air have been withdrawn, the potassa rises in the other limb of the tube to a higher level than in the rest of the apparatus, and maintains its level for some time, it is a proof that the apparatus is air-tight.

The tube is now gradually and carefully heated throughout its whole length, commencing in front, with red-hot charcoal, the fire being regulated with a regard to the rapidity of the passage of bubbles through the potassa-apparatus.

When the fire is carried to the hinder extremity of the tube, pure oxygen will be disengaged from the mixture of the chlorate of potassa and chromate of lead, and will sweep the whole of the carbonic acid out of the tube. At the conclusion, the fire is raised by fanning with a millboard-fan, and the heat continued as long as any bubbles of gas are evolved; the operation is terminated by nipping off the extreme point of the tube, and the potassa-bulbs are then detached and weighed.

The increase of weight of the potassa-apparatus after the experiment, indicates the amount of carbonic acid produced, since the phosphorus and sulphur have remained in the tube in their highest states of oxidation.

Calculation.

$$\begin{array}{l} CO_2 \quad C \\ 22 \quad : \quad 6 \quad :: \text{Weight of carbonic acid} : x \\ x = \text{Weight of carbon.} \end{array}$$

Determination of uncombined Carbon and Silicon.—About 100 grains of the iron filings are gently heated with dilute hydrochloric acid, until all action has ceased, the residue, consisting of particles of graphite and silica, is collected upon a small weighed filter, well washed, and dried. A little ether is then poured over it, to remove any oily hydrocarbons which might have adhered, the filter again dried at 212° F., and weighed. It is then incinerated in the usual manner, the combustion of the graphite being effected in a current of oxygen. When the weight of the filter-ash is deducted, the amount of the silica is known, and must be subtracted from that of the original residue, to obtain the weight of the uncombined carbon.

¹ A method which should include the rare metals contained in cast-iron would be far too laborious to be generally adopted for practice.

If any silica is contained in the solution, it may be determined in the usual manner (p. 594).

Determination of Iron, Manganese, Calcium, and Sodium.—The filtrate from the silica is heated with nitric acid, in order to peroxidize the iron, the excess of acid evaporated, and, at the same time, the solution concentrated to a small bulk, and the iron separated as succinate or benzoate (p. 586).

The solution filtered from the iron-precipitate is evaporated to dryness, and the residue heated, to expel ammoniacal salts. It is then dissolved in hydrochloric acid, a slight excess of ammonia added, then some sulphide of ammonium, the solution allowed to stand for some hours, and gently heated. The precipitated sulphide of manganese is filtered off, and treated as at p. 588.

The lime in the filtrate is precipitated as oxalate (p. 590).

The filtrate from the oxalate of lime is carefully evaporated to dryness, the residue ignited, and the sodium determined as chloride (p. 591).

Determination of Sulphur.—A considerable quantity of the iron (varying with the amount of sulphur present) is dissolved, in a large flask, in fuming nitric acid, the solution evaporated to expel the greater excess of acid, largely diluted with water, and the sulphuric acid precipitated as sulphate of baryta, which must be very well washed with boiling water (p. 592), dried, ignited, and weighed.

Determination of the Phosphorus.—The iron is dissolved in *aqua regia*, the solution carefully evaporated to dryness to expel excess of acid, the residue treated with water, and mixed with a considerable excess of hydrosulphate of sulphide of potassium, with which it is digested, at a temperature approaching the boiling-point, for several hours, when the iron and manganese are entirely converted into sulphides, and the phosphoric acid passes into solution. The latter is mixed with a slight excess of hydrochloric acid, to decompose the excess of sulphide of potassium, the solution boiled until no more sulphuretted hydrogen is evolved, filtered, if necessary, from the separated sulphur, and the phosphoric acid determined as phosphate of iron (p. 593).

ULTRAMARINE.

(The artificial pigment is to be employed.)

§ 439. The chief constituents of ultramarine are: *silica, sulphuric acid, sulphur, alumina, soda, lime, oxide of iron.*

The pigment is dried in the water-bath till its weight ceases to vary.

Determination of Sulphur.—About 20 grains of the compound are oxidized, as usual, with the strongest nitric acid, and the sulphur determined as sulphate of baryta, from the weight of which must be deducted that of the sulphate of baryta furnished by the sulphuric acid already existing in the compound.

Determination of the Remaining Constituents.—About 50 grains are boiled with concentrated hydrochloric acid, in a flask; the solution together with the residue of silica, transferred to a dish and carefully evaporated to dryness in the air-bath; the dry mass is digested with dilute hydrochloric acid, the silica filtered off and determined as usual.

The filtrate and washings are evaporated to a small bulk, introduced into a dry weighed flask, and the weight of the solution determined. About one-fourth of the solution is then poured into a beaker, and the sulphuric acid determined as sulphate of baryta. The flask, with the remainder of the solution is again weighed, and then the amount which has been employed is determined.

The remainder of the solution is boiled with nitric acid, to peroxidize the iron, mixed with ammonia in excess, and the precipitated alumina and sesquioxide of iron determined (if the amount of the latter be sufficient) as in the analysis of clay (p. 605).

The lime is precipitated from the filtrate as oxalate, and the soda subsequently determined as chloride of sodium.

SEPARATION OF CHLORINE, BROMINE, AND IODINE.

§ 440. It occasionally happens, in the analysis of mineral waters, &c., that a mixed precipitate is obtained, containing chloride, bromide, and iodide of silver, in which it is required to determine the amount of each salt-radical.

For this purpose, a convenient quantity of the precipitate is dried, well mixed, so that it may be perfectly homogeneous, and introduced into a weighed bulb-tube of hard glass, in which it is fused, and its weight determined.

The bulb-tube is then connected with a small retort from which a current of bromine-vapor can be passed through the tube; a delivery-tube is attached to the bulb-tube, so that the excess of bromine may be passed into solution of potassa. The precipitate is fused in an atmosphere of bromine, the tube being repeatedly turned to expose a fresh portion of the precipitate to the action of the vapor, until its weight no longer varies. The bromine has then entirely replaced the iodine, the amount of which may be calculated from the difference of weight. Of course, all the bromine must be carefully expelled from the tube, and replaced by air previously to weighing.

By a similar operation in a current of dry chlorine, the bromine may be displaced.

Calculation.

$$\begin{array}{l} \text{Difference between} \\ \text{eqs. of I and Br.} \end{array} \quad \begin{array}{l} I \\ 127.1 \end{array} \quad \begin{array}{l} : \\ :: \end{array} \quad \begin{array}{l} \text{1st difference of weight} : x \\ x = \text{Weight of iodine.} \end{array}$$

1). 47.1

$$\begin{array}{l} \text{Difference between} \\ \text{eqs. of Br. and Cl.} \end{array} \quad \begin{array}{l} Br \\ 80.0 \end{array} \quad \begin{array}{l} : \\ :: \end{array} \quad \begin{array}{l} \text{2d difference of weight} : y \\ y = \text{Weight of Bromine originally present, together with that which has replaced} \\ \text{the iodine.} \end{array}$$

2). 44.5

The amount of bromine equivalent to the iodine present must be calculated, and subtracted from *y*.

The joint weight of the bromide and iodide of silver is calculated, and subtracted from that of the original precipitate, in order to ascertain the weight of the chloride of silver.

A very accurate method of separating chlorine, bromine, and iodine, when existing in solution, is executed as follows:—

The solution is mixed with nitrate of palladium as long as any precipitate is formed; the mixture is set aside for 12 hours, the brownish-black iodide of palladium collected upon a weighed filter, washed with warm water, and dried, at a temperature which must not exceed 176° F. (80° C.), until its weight is constant.

Calculation.

$$\begin{array}{l} PdI \\ 180.4 \end{array} \quad \begin{array}{l} I \\ 127.1 \end{array} \quad \begin{array}{l} : \\ :: \end{array} \quad \begin{array}{l} \text{Weight of precipitate} : x \\ x = \text{Weight of iodine.} \end{array}$$

The chlorine and bromine are precipitated from the filtrate with nitrate of silver, and their relative amounts determined by heating a portion of the precipitate in a current of chlorine.

ANALYSIS OF WATERS.

§ 441. Since the number of substances generally contained in waters is limited, their analysis is usually effected by a special method.

The following list includes those substances which most frequently occur in waters:—

<i>Bases.</i>	<i>Acids.</i>
Potassa	Sulphuric
Soda	Phosphoric
Lime	Silica
Magnesia	Carbonic
Alumina	Nitric
Oxide of iron	Hydrochloric
	Hydrosulphuric
Organic matters.	

Lithia, ammonia, strontia, oxide of manganese, oxide of lead, hydriodic acid, hydrobromic acid, and hydrofluoric acid, so rarely occur, that they are not considered in the general plan for the analysis.

QUALITATIVE ANALYSIS.

This portion of the examination may be divided into

1. That of the *original water*, which should embrace the detection of hydro-sulphuric acid, of free carbonic acid, and of organic matter, together with the determination of the reaction to test-papers, and the rough test of the hardness of the water.
2. That of the *precipitate produced by evaporation*, which should be examined for the *carbonates of lime and magnesia, sulphate of lime, sesquioxide of iron, silicic acid.*
3. The analysis of the *filtrate*, in which there should be sought *all bases,¹ silicic acid, sulphuric acid, hydrochloric acid, nitric acid, phosphoric acid, carbonic acid.*

Waters should be analyzed as soon as possible after they are taken from the source, whence they should be collected in stoppered bottles, which must be quite filled with the water. Corks very soon reduce the sulphates in the water to the state of sulphides.

Forty ounces of the water are usually sufficient for a qualitative analysis for practical purposes.

Examination of the original Water.—1. A little of the water is placed in a test-tube, and a slip of violet litmus-paper (to show both acids and alkalis) introduced; after standing for some time, the paper is compared with another piece of the same kind, which has been soaked for a like period in distilled water.

2. About two fluidounces of the original water are evaporated to dryness in a porcelain dish, and the residue heated; it is to be observed whether considerable charring takes place, and whether any odor of *nitrogenized organic matter* is evolved.

3. The presence of *sulphuretted hydrogen* in the water is ascertained by the odor, and by the production of a black or gray precipitate with acetate of lead.

4. In order to detect the *free carbonic acid*, about half an ounce of the water

¹ This is recommended, because the trouble involved is very slight, and may sometimes lead to the discovery of a base (*lead*, e. g.) which would otherwise be passed over.

is gradually heated in a large test-tube, when bubbles of carbonic acid will be evolved.

Or the water is poured into a little lime-water, when the free carbonic acid produces a white precipitate, which redissolves on adding a large quantity of the water.

5. In order roughly to test the *hardness* of waters, they are mixed with a few drops of an alcoholic solution of white soap, when a white precipitate of greater or less quantity will make its appearance.

As much of the water as can be conveniently spared is evaporated to about $\frac{1}{8}$ its original volume, and the *solution* filtered off from the *precipitate*.

Examination of the Filtrate.—The examination for *bases* is conducted as usual.

Examination for Acids.—*Silicic acid* will be detected in the examination for *bases*.

(The reaction of this filtrate to test-papers should be tried; if it be alkaline, *fixed alkaline carbonates* are contained in the water).

To one portion of the solution chloride of barium is added; a white precipitate may consist of sulphate, carbonate, or phosphate of baryta. Dilute hydrochloric acid is added.

Sulphate of baryta would be left undissolved, indicating the presence of *sulphuric acid*. Phosphate and carbonate of baryta would be dissolved, the latter with effervescence.

Another portion of the solution is mixed with nitrate of silver; the precipitate may consist of chloride of silver (white), carbonate of silver (white), or phosphate of silver (yellow). Dilute nitric acid is added.

Chloride of silver would be left undissolved, indicating the presence of *hydrochloric acid*.

Another portion of the solution is tested for phosphoric acid by acidifying slightly with acetic acid, and adding a single drop of sesquichloride of iron; a white precipitate of phosphate of sesquioxide of iron indicates the presence of *phosphoric acid*.

Another portion of the solution is mixed with half its bulk of concentrated sulphuric acid (perfectly free from nitric acid), allowed to become nearly cool, and a crystal of sulphate of iron dropped into it. After standing for some time, at perfect rest, the presence of *nitric acid* will be indicated by a brown halo around the crystal.

Examination of the Precipitate produced by Evaporation.—This precipitate is dissolved in warm dilute hydrochloric acid (which should be rinsed round the dish, and then poured over the filter). The presence of *carbonic acid* will be indicated by the effervescence.

The greater part of the solution is evaporated to dryness, and the residue treated with dilute hydrochloric acid. Insoluble white flakes consist of *silica*.

The solution filtered from the silica is mixed with ammonia in excess. A red-brown precipitate consists of *sesquioxide of iron*.

The filtrate is gently heated with carbonate of ammonia. A precipitate of carbonate of lime will be formed if *lime* be present.

The filtered liquid is mixed with phosphate of soda, violently agitated, and allowed to stand for 24 hours. A white crystalline precipitate of phosphate of *magnesia* and ammonia indicates the presence of *magnesia*.

The remainder of the hydrochloric solution is tested for *sulphuric acid* with chloride of barium.

The points which it is generally important to determine in the quantitative analysis of mineral waters are:—

The *total weight of solid matter* contained in the water;

The total amounts of *potassa, soda, lime, magnesia, oxides of iron, sulphuric acid, silicic acid, carbonic acid, chlorine, organic matter*;

The amounts of *lime, magnesia, and sesquioxide of iron contained in the precipitate*;

The *degree of hardness* of the water;

The *specific gravity* of the water

The constituents are generally calculated for an imperial gallon (70,000 grs.) of distilled water.

Moreover, when the water contains *alkaline carbonates*, we generally desire to ascertain their amount.

Also, when *sulphuretted hydrogen* is present, its quantity must be determined.

About eight pints of water will usually suffice for a quantitative analysis; but since it is generally necessary to conduct two analyses at once, for the sake of a control, twice this quantity ought to be provided.

In the subsequent analysis the water may either be measured or weighed; the latter should be preferred as more accurate, when it is practicable.

For measuring the water, a flask should be employed with a mark on the neck showing the height to which it is filled by a weighed amount of water.

Determination of the Specific Gravity of the Water.—A stoppered bottle, capable of containing about four ounces, is dried¹ and weighed. It is then exactly filled with the water, the temperature of which is carefully noted, and again weighed.

Lastly, after rinsing, it is filled with distilled water of the same temperature, and its weight again determined.

The specific gravity is then obtained by dividing the weight of the water examined by that of the distilled water.

This determination of the specific gravity serves as a basis for the calculation of the actual weight of an imperial gallon of the water; for as

$$1 : \text{Sp. gr. of the water} :: 70,000 \text{ grs.} : x$$

$$x = \text{Weight of an imperial gallon of the water in grains.}$$

It is only necessary, therefore, to multiply the specific gravity by 70,000, in order to obtain the weight of the imperial gallon of the water in grains.

Determination of the Total Weight of Solid Matter.—About 4,000 grs. of the water are weighed in a flask, whence they are transferred to a beaker, which is covered with an inverted funnel, and heated on a sand-bath till no more bubbles of carbonic acid are evolved. The water is then evaporated, by successive portions, in a weighed platinum dish placed in an air-bath; any precipitate which may have been deposited in the beaker is carefully rinsed out into the dish; the evaporation is carried to dryness, and the dry residue heated to about 320° F. (160° C.) in the air-bath till its weight is constant.

Calculation.

$$\text{Weight of water employed} : \text{Residue obtained} :: \text{Weight of an imp. gall.} : x$$

$$x = \text{Amount of solid matter in an imperial gallon.}$$

Determination of Organic Matter.—The above dry residue is carefully incinerated, till perfectly white (p. 573), at as low a temperature as possible; it is then moistened with carbonate of ammonia (to recarbonate any lime), dried in the air-bath, and weighed. The loss of weight represents the quantity of organic matter, which should be calculated upon a gallon of the water, and deducted

¹ In order to dry such a flask, it should be gently heated, and the contained air sucked out repeatedly with a tube.

from the total weight of solid ingredients, in order to ascertain the amount of inorganic matter contained in a gallon.

Determination of the Lime, Magnesia, and Iron.—About 12,000 grs. of the water are accurately weighed, introduced into a large flask, and heated with excess of nitric acid until all the carbonic acid is expelled. The solution is then evaporated to a small bulk in a porcelain dish placed upon a sand-bath, transferred to a small dish, and the evaporation carried to perfect dryness in an air-bath. The dry residue is digested with dilute hydrochloric acid, the residual silica filtered off, well washed, dried, ignited, and weighed. The iron is precipitated from the filtrate (previously concentrated) by ammonia, the lime subsequently, as oxalate, and the magnesia determined as pyrophosphate. The filtrate should, in each case, be concentrated before precipitation.

The amounts of lime and magnesia are calculated for an imperial gallon of water.

The sesquioxide of iron is reckoned as protoxide, and calculated for an imperial gallon of water.

Determination of the Lime, Magnesia, and Iron, in the Precipitate produced by Boiling.—About 12,000 grs. of the water are accurately weighed, and boiled, in a flask, for about an hour, taking care to preserve the same quantity of water, by adding distilled water from time to time, so that no sulphate of lime may be precipitated.

The solution is filtered off, the precipitate well washed upon the filter, and dissolved with very dilute hydrochloric acid, which should be also rinsed round the flask, to dissolve any adhering particles of the precipitate.

The acid solution is boiled with a little nitric acid, and the sesquioxide of iron, lime, and magnesia, separated and determined as usual.

The amount of each of these constituents is then calculated for an imperial gallon of the water (the sesquioxide of iron being reduced to oxide), and deducted from the total amount found in the preceding determination. The differences express the amounts of oxide of iron, lime, and magnesia, existing in the water uncombined with carbonic acid.

The quantities of carbonic acid required by the oxide of iron, lime, and magnesia, found in the precipitate, are then calculated, and added to the weights of the three oxides existing as carbonates in the imperial gallon; the sums represent the amounts of the carbonates of oxide of iron, lime, and magnesia, existing in an imperial gallon of water.

Determination of Potassa and Soda.—About 9000 grs. of the water are accurately weighed, evaporated in a beaker to about $\frac{1}{2}$ of their bulk, and mixed with a little chloride of barium and excess of baryta-water; the solution is gently heated, the precipitate allowed to subside, filtered off, and well washed.

The filtrate and washings are again evaporated to a small bulk, and gently heated with ammonia and carbonate of ammonia, to precipitate the baryta and lime which are filtered off; the filtrate is then evaporated to dryness in a small weighed dish, and carefully ignited to expel ammoniacal salts. The residual chlorides of potassium and sodium are weighed, and separated as in the analysis of Rochelle salt (p. 602). The amount of each metal is then calculated for an imperial gallon of the water.

Determination of Sulphuric Acid.—About 9000 grs. of the original water are acidified with hydrochloric acid, and the sulphuric acid precipitated as sulphate of baryta, which is allowed 24 hours to subside, and determined as directed at p. 592. Its amount is then calculated for an imperial gallon.

Determination of Chlorine.—About 5000 grs. of the water are acidulated with nitric acid, and the chlorine determined as chloride of silver (p. 597). The amount of chlorine in an imperial gallon is then calculated.

Determination of the total amount of Carbonic Acid.—This can only be

effected with absolute accuracy when the analyst has access to the source of the water.

It is then necessary to provide himself, beforehand, with the following apparatus, &c.

A glass vessel, of suitable form, capable of containing about 12 ounces; its capacity must be accurately known. The best form for this vessel is that of an adapter (of course open at both ends), and so narrow at the top as to admit of its being closed with the thumb, so that it may be dipped into the spring, a certain quantity of water withdrawn in it, by closing it with the thumb, and the water allowed to run into the bottles by merely removing the thumb from the orifice. This instrument is sold under the rather inappropriate name of a *siphon for mineral waters*.

Four or five *stoppered bottles*, capable of holding about 16 ounces.

A few ounces of a clear solution of *chloride of calcium*.

A small quantity of *ammonia* which does not give any precipitate with chloride of calcium.

When at the spring, the operator must introduce about an ounce of solution of chloride of calcium, and an ounce of ammonia, into each of the bottles. A siphon-full of water is then placed in each of the bottles, which are then closely stopped and removed to the laboratory. The precipitates are collected upon a weighed filter, dried at 212° F. and weighed. The dry precipitate is well mixed, to insure its uniformity, and the carbonic acid in a weighed portion of it determined (p. 596). Two or three determinations may be made, to control each other.

The amount of carbonic acid is then calculated for the whole precipitate, and subsequently for an imperial gallon of water.

By deducting, from the total quantity of carbonic acid, that combined with the lime, magnesia, and oxide of iron (previously determined), we ascertain the amount of free carbonic acid present (unless there be any alkaline carbonates).

The *degree of hardness* of a mineral water is determined by *Clark's soap-test*, which consists in ascertaining the quantity of a standard solution of soap in spirit, required to produce a permanent lather with a given quantity of the water under examination, the result being expressed in degrees of hardness, each of which corresponds to one grain of carbonate of lime in a gallon (= 70,000 grs. of distilled water) of water.

The soap-solution is prepared by dissolving curd soap (*Hawes's white-curd*) in proof spirit, in the proportion of about 120 grs. to a pint. In order to graduate this solution, 16 grs. of pure carbonate of lime (calcareous spar, white marble) are dissolved, without loss, in a small quantity of hydrochloric acid; the solution is very carefully evaporated to dryness in an air-bath, the residue redissolved in water, the solution again evaporated, and these operations repeated until a perfectly neutral solution has been obtained.

The neutral solution of chloride of calcium thus prepared is to be diluted with so much distilled water as will make up a gallon; it will then represent a water of 16° hardness. 100 measures¹ of this solution are introduced into a stoppered bottle capable of containing 2,000 grains, and the soap-solution is very gradually added to it from a burette (the stopper being replaced, and the solution violently agitated from time to time), until a lather is formed which remains for five minutes over the whole surface of the liquid, when the bottle is laid down upon the table. The number of measures of soap-solution used is then noticed, and the strength of the solution altered, if necessary, by a further addition either of soap or spirit, until exactly 32 measures of the liquid are required for 100 measures of the water of 16° hardness.² The trial should then be repeated, in

¹ Each measure is equal to 10 grs. of distilled water.

² This standard soap-solution may be purchased at the operative chemist's.

exactly the same way, with the water of 16° hardness, in order to leave no doubt of the strength of the soap-solution.

To apply this test, the water to be examined is introduced into a stoppered bottle, which should be half filled with it, and violently agitated, in order to disengage any free carbonic acid, which would increase the quantity of soap required to form a lather; the air in the bottle is then sucked out through a glass tube, and these operations repeated two or three times, until it is judged that the free carbonic acid is entirely removed. 100 measures of this water are then introduced into a stoppered bottle of twice that capacity, and treated as in the case of the artificial water of 16° hardness (*see above*), except that the carbonic acid should be sucked out at intervals from the upper part of the bottle. The hardness of the water is then inferred directly from the number of measures of soap-solution employed, by reference to the subjoined table.

If the water is so hard that 32 measures of the soap-solution do not yield a permanent lather, 100 measures of distilled water are added, and the experiment proceeded with in the usual manner, until 60 measures of soap-solution have been used. Should these fail to produce a lather, 100 measures of distilled water are again added, and the operation conducted until 90 measures of soap-solution have been taken; if more soap is even then necessary, its addition must be preceded by that of 100 measures more distilled water. When a lather has been obtained, another experiment is commenced with a mixture of 100 measures of the original water, with the total quantity of distilled water added in the preceding determination. The number of measures of soap-solution used, must be divided by the number of 100 measures contained in the mixture, and the degree of hardness corresponding to the quotient having been found by reference to the table, it must be multiplied by the former divisor, to obtain the true degree of hardness. Thus, if the original water had been diluted with 200 measures of distilled water, and had then required 96 measures of soap solution, it would be necessary to divide 96 by 3, and to refer the quotient 32, to the table, where it would be seen to correspond to 16°, which, multiplied by 3, gives 48° for the actual hardness of the water.

If very accurate results be desired, it is recommended to shake the water, to which a sufficiency of soap-solution has been added, at intervals of half an hour, and, should the lather not then continue for five minutes, to add as much more soap-solution as is necessary to produce that effect, even after standing for such a period.

<i>Degree of hardness.</i>	<i>Measures of Soap-solution.</i>	<i>Differences for the next 1° of hardness.</i>
0° (Distilled water)	1.4	1.8
1	3.2	2.2
2	5.4	2.2
3	7.6	2.0
4	9.6	2.0
5	11.6	2.0
6	13.6	2.0
7	15.6	1.9
8	17.5	1.9
9	19.4	1.9
10	21.3	1.8
11	23.1	1.8
12	24.9	1.8
13	26.7	1.8
14	28.5	1.8
15	30.3	1.7
16	32.0	

When the number of measures of the soap-solution fall between any two numbers given in the table, the hardness will be expressed, of course, by an integer and a fraction; the integer will be the degree of hardness corresponding to the next lower number in the soap-test column; the numerator of the fraction will be found by subtracting this last number from the actual number of measures employed; and the denominator will be the difference, in the third column, corresponding to the number above referred to in the second column; thus, if 25.8 measures of the soap-solution have been employed, the number 12, opposite to the next lower number, 24.9, in the soap-test column, represents the integral part of the hardness; the numerator of the fractional part is $25.8 - 24.9 = 0.9$, and the denominator is 1.8, the difference corresponding to 24.9; the fraction, then, is $\frac{0.9}{1.8} = 0.5$, and 12.5 is the hardness required.

According to Clark, the hardness of a water may be inferred from an ordinary analysis, by calculating the total amount, in grains, of carbonate of lime, equivalent to the lime, magnesia, oxides of lime, and alumina, in a gallon of water; the number thus obtained will represent the hardness, in degrees.¹

To determine the amount of alkaline carbonate present in a water, the following method is adopted: About 5000 grains of water are boiled for a considerable time, the precipitate filtered off, and well washed. The filtrate is divided into two parts, both of which are accurately weighed. In the one portion, the chlorine is determined as usual. The other is acidified with hydrochloric acid, evaporated to dryness, gently ignited, and the chlorine determined in the aqueous solution of the residue.

The difference between this quantity of chlorine and the former (calculated upon the same quantity of liquid) expresses the amount of chlorine corresponding, equivalent for equivalent, to the alkali present in the form of carbonate.

The sulphuretted hydrogen contained in a water should, if possible, be determined at the spring.

Three or four stoppered bottles are taken, and into each of them a small quantity of a solution of arsenious acid in hydrochloric acid is poured. A siphon-full of water is then introduced into each bottle (as in the determination of carbonic acid). In order to ascertain the amount of the sulphuretted hydrogen, the precipitated tersulphide of arsenic is collected upon a filter of known weight, well washed, dried at 212° F., and weighed.

The amount of sulphuretted hydrogen is then calculated for an imperial gallon.

It is usual to arrange the results of the analysis of a water according to the following general rules (Fresenius); the equivalent numbers are, of course, the data for the calculations:—

1. The lime, magnesia, and protoxide of iron, in the precipitate by boiling, are calculated and stated as carbonates, the carbonic acid which they require being calculated, and deducted from the total amount of carbonic acid present.

The remainder is stated as free carbonic acid (unless alkaline carbonates are present).

2. The rest of the lime is calculated and stated as sulphate. The sulphuric acid which it requires is calculated and deducted from the total amount of sulphuric acid; the remainder, if any, is calculated as sulphate of potassa, and should any still remain, it is calculated as sulphate of soda.

3. The rest of the sodium is calculated as chloride.

¹ Campbell has made some experiments on the action of the soap-test upon waters containing magnesia, from which he has deduced the following conclusions: 1. That the magnesia, in its behavior to the soap-test, is equivalent to lime, only when its amount does not correspond to more than six grains of lime in a gallon of water. 2. That, for many waters, Clark's rule for calculating the hardness from an ordinary analysis, is not accurate.

4. The remainder of the chlorine is calculated as chloride of magnesium; should any magnesium remain, it must exist as sulphate.

It is obvious that this method of calculation will afford a valuable control for the analysis.

Moreover, the sum of the various inorganic constituents (the iron being calculated as sesquioxide) should be nearly equal to that of the total amount of inorganic matter determined by evaporation.

The amount of alkali existing in the water as carbonate has been determined previously.

ANALYSIS OF SOILS.

§ 442. The following substances are generally found in soils:—

<i>Bases.</i>	<i>Acids.</i>
Potassa	Sulphuric
Soda	Phosphoric
Ammonia (<i>rarely</i>)	Silicic
Lime	Carbonic
Magnesia	Hydrochloric
Alumina	Nitric (<i>rarely</i>)
Oxide of manganese	Hydrofluoric (<i>rarely</i>)
Oxide of iron	
Sesquioxide of iron	
	Organic matter.

Traces of copper, arsenic, &c. have occasionally been detected.

The specimens of soil should be taken at different depths, and from different parts of the field; they should be uniformly mixed, all large stones, roots, &c., picked out, and the soil spread upon a sheet of paper and allowed to dry spontaneously in the air for a day or two; it is then powdered in a mortar, and rubbed, with the fingers, through a piece of muslin stretched over the mouth of a beaker.

Preliminary Examination of the Soil.—1. A portion of the soil is heated on platinum to ascertain whether much *organic matter* is present, which may be known by the carbonization, and whether there is any *nitrogenized organic matter*, known by the odor of burnt hair which it emits when heated.

2. Another portion is mixed with hydrate of lime, in a dish, the mixture moistened with water, and very gently heated, to test for *ammonia*.

If the soil be found to contain a large quantity of organic matter, it should be very gently ignited previously to examination, and, in this case, nitric and carbonic acids must be sought in the unignited soil; after ignition we must expect to find some of the sulphate of lime reduced to sulphide of calcium, and the sesquioxide of iron reduced to oxide.

It must be remembered that our object in analyzing a soil is not merely to ascertain what substances are present, but also to determine the condition in which they are contained in the soil, whether they are soluble or insoluble; whether, for example, the lime is present as sulphate or as carbonate; whether the alkalies are soluble and ready to be absorbed by the plant, or whether they exist in the form of insoluble silicates, which are, at present, useless.

The examination of the soil must therefore be divided into three parts:—

1. Analysis of the *portion soluble in water*.
2. Analysis of the *portion soluble in hydrochloric acid*.
3. Analysis of the *insoluble residue*.

QUALITATIVE ANALYSIS.

Examination of the portion soluble in Water.—About eight ounces of the soil are boiled, in a dish, with a pint of water, for half an hour, and filtered.

The filtrate is evaporated to about one ounce, and divided into two parts.

One portion is examined as usual for bases.

The other portion is tested in the ordinary manner, for sulphuric, phosphoric, hydrochloric, and nitric acids.

Examination of the portion soluble in Hydrochloric Acid. About $\frac{1}{2}$ of the residue left by water is introduced into a flask, and boiled, for about ten minutes, with concentrated hydrochloric acid; water is then added, the boiling continued for some time, and the solution filtered. (If the residue effervesced when treated with hydrochloric acid, it indicates the presence of carbonic acid.)

A small portion of the hydrochloric solution is tested with chloride of barium, for sulphuric acid.

Another small portion is set aside.

The greater part of the hydrochloric solution is examined for bases and for phosphoric acid according to the general process.

Examination of the insoluble Residue.—This residue is dried and divided into two parts.

One part is analyzed according to Table VIII.

The other portion is examined for alkalies according to Table VIII.

A portion of the original soil may be tested for hydrofluoric acid by the terfluoride of silicon test (p. 536).

A portion of the original soil should be ignited and tested for manganese, by fusion with carbonate of soda and nitre.

QUANTITATIVE ANALYSIS.

The method here given for the quantitative analysis of soils, will include the determination of the following substances: potassa, soda, lime, magnesia, alumina, oxide of manganese, oxide and sesquioxide of iron, sulphuric, phosphoric, silicic, carbonic, and hydrochloric acids, organic matter, and water.

Determination of Water.—About 250–300 grains of the air-dried soil, are heated in a water-bath till the weight is constant. The loss represents the amount of water.

Determination of Organic Matter.—About 50 grains of the perfectly dried soil are introduced into a platinum crucible, accurately weighed, and completely incinerated with the usual precautions (p. 573). The residue is allowed to cool, moistened with sesquicarbonate of ammonia (to recarbonate any caustic lime), and dried in an air-bath, at a little above 212° F. till its weight is constant.

The loss indicates the total quantity of organic matter in the dry soil, which is then calculated for 100 parts of air-dried soil.

Determination of the total amount of Carbonic Acid.—About 50 grains of the air-dried soil are employed for the determination of carbonic acid by the method of Fresenius and Will (see p. 596).

Determination of the total amount of Constituents soluble in Water.—From 500 to 600 grains of air-dried soil are heated with four or five ounces of water, in a beaker, for a considerable period, nearly to ebullition; the residue is allowed to subside perfectly, the solution poured through the filter, and the residue again heated with water; this operation is repeated, till a few drops of the solution do not leave any considerable residue when evaporated on platinum.

The residue is thrown upon a weighed filter, washed with hot water till the washings leave no appreciable residue when evaporated, dried in a water-bath, and weighed.

By deducting the weight of this residue from that of the air-dried soil employed, and subtracting from the result the amount of water known to be present in the air-dried soil, we ascertain the total quantity of the soluble ingredients.

It is well to control this result by evaporating the filtrate and washings, first, in a porcelain basin upon a sand-bath, then, in a weighed platinum capsule, placed on a water-bath, to dryness, and heating the residue in a water-oven till its weight is constant. The total quantity of soluble matter is then calculated for 100 parts of the air-dried soil.

Determination of the amount of Organic Matter soluble in Water.—The residue obtained in the above experiment is gently ignited till all organic matter is burnt off. The loss of weight indicates the amount of soluble organic matter present.

Determination of the Individual Constituents soluble in Water.—(Should a large amount of organic matter be present, it is better to destroy it by moderately heating the weighed portion of the soil, before proceeding with the subsequent operations.)

An accurately weighed¹ quantity of the soil (which must be varied according to the number of constituents to be determined in the solution, about 1500 grains being usually sufficient) is introduced into a beaker, and treated with water exactly as directed for the determination of the total amount of solid matter, except that the residue may be collected on an ordinary (not weighed) filter.

The solution and washings are evaporated till they do not measure more than 10 or 12 ounces, introduced into a dry weighed flask, and accurately weighed.

Determination of the Bases (except Alkalies).—(It very rarely happens that the aqueous solution contains a sufficient quantity of alumina, manganese, iron, or of silica or phosphoric acid, for quantitative estimation; should this, however, be the case, their separation and determination may be effected by the ordinary methods.)

About one-fifth of the aqueous solution is poured into a beaker, and the flask afterwards accurately weighed to ascertain the amount of solution which has been taken.

The lime is then determined, in the usual manner, as oxalate, and, subsequently, the magnesia in the filtrate, as pyrophosphate.

The amounts of lime and magnesia are calculated for the whole of the solution, and thence, for 100 parts of the air-dried soil.

Determination of the Alkalies.—The alkalies are determined in two-fifths of the aqueous solution by the method given for their determination in waters, p. 681.

Determination of Sulphuric Acid.—The sulphuric acid is determined in another fifth of the aqueous solution, as sulphate of baryta.

Determination of Chlorine.—The remaining fifth of the solution is employed for the estimation of chlorine as chloride of silver.

Determination of the Constituents soluble in Hydrochloric Acid.—The residue left on boiling the weighed portion of soil with water is dried on the filter by exposure in a warm situation, detached, as far as possible, from the filter, well powdered, and dried, for an hour or two, at 212° F.

About 500 grains of this residue (accurately weighed) are introduced into a platinum dish, and gently ignited till all organic matter is perfectly destroyed, and the mass completely incinerated. The residue is then transferred to a large flask, covered with water, and concentrated hydrochloric acid gradually added till all effervescence has ceased; a little more hydrochloric acid is then added, mixture boiled for about an hour, upon a sand-bath, allowed to subside, the

¹ The soil may be conveniently weighed in a light beaker.

clear liquid carefully poured off into a beaker, and the residue once more boiled, for a few minutes, with a fresh portion of hydrochloric acid. The clear liquid is again decanted, mixed with the first portion, the whole diluted with water, and filtered through a weighed filter. The residue in the flask is thrown on to the filter, and washed till the washings have no longer an acid reaction.

The solution and washings are mixed with a little nitric acid, and carefully evaporated to dryness, in an air-bath, the residue moistened with concentrated hydrochloric acid, then digested with dilute hydrochloric acid for some time. The undissolved silica is collected upon a filter, and determined in the usual manner (p. 594).

The filtrate and washings are concentrated by evaporation, introduced into a stoppered bottle, and accurately weighed.

The amount of silica obtained is calculated for the quantity of aqueous residue employed, and subsequently, for the quantity of this residue which is known to correspond to 100 parts of the air-dried soil.

Determination of the Bases (except the Alkalies), and of Phosphoric Acid.—

About one-half of the hydrochloric solution (accurately weighed), is gradually mixed with ammonia, with constant stirring, until a precipitate begins to appear, which does not redissolve entirely on stirring; a gentle heat is then applied, and when the precipitate has redissolved, some acetate of potassa is added until the liquid has a distinct red color (should there be not enough iron for this purpose, a little sesquichloride of iron should be added¹). The mixture is introduced into a capacious porcelain dish, and boiled till the liquid portion has lost its red color, denoting that all the acetate of sesquioxide of iron is decomposed; the solution is then filtered while hot, and the precipitate washed with hot water.

The precipitate, which contains alumina, sesquioxide of iron, and phosphoric acid, is dissolved off the filter in warm dilute hydrochloric acid (the filter being well washed); the solution is mixed with ammonia till a permanent precipitate begins to form, and sulphide of ammonium added in excess. The mixture is digested for an hour or two at a moderate heat, the precipitate (sulphide of iron and, perhaps, of manganese and alumina, with a little phosphoric acid) filtered off and washed with water containing sulphide of ammonium.

The filtrate and washings (containing most of the phosphoric acid) are evaporated to a small bulk, acidulated with hydrochloric acid, and heated with a little concentrated nitric acid to oxidize and dissolve the separated sulphur. The phosphoric acid is then determined in the solution as basic perphosphate of iron (p. 593).

The precipitate, containing sulphide of iron, and perhaps, of manganese and alumina, is dissolved in hydrochloric acid, the solution heated till all sulphuretted hydrogen is expelled, boiled with a little nitric acid, and mixed with the acetic solution originally filtered off from the precipitate containing phosphoric acid.

The solution is concentrated, if necessary, by evaporation, mixed with chloride of ammonium and excess of ammonia, heated, and filtered.

The lime and magnesia in the filtrate are determined as usual.

The precipitate, which contains alumina, iron, and manganese, is treated exactly as in the analysis of clays (p. 605); the ignited precipitate, containing only iron and manganese, is subsequently dissolved in hydrochloric acid, and the iron and manganese separated and determined by the method employed in the analysis of cast-iron (p. 626).

The results are all calculated upon 100 parts of air-dried soil, the iron and manganese being calculated as peroxides.

Determination of Alkalies.—About one-fourth of the hydrochloric solution is

¹ In this case, which seldom occurs, the iron must of course be determined in another portion.

evaporated to dryness in an air-bath, the residue stirred, and heated with water, an excess of baryta-water added, the solution again heated for some time, and filtered; the filtrate is then treated as directed for the determination of alkalies in the aqueous solution.

The alkalies are calculated for 100 parts of air-dried soil.

Determination of Sulphuric Acid.—This acid will only occur in the hydrochloric solution when the washing of the aqueous residue has been incomplete. It is determined as sulphate of baryta.

Analysis of the portion insoluble in Water and Acids.—This residue is dried in the water-bath, till its weight is constant.

Determination of Silicic Acid and of all Bases except Alkalies. This is conducted according to the method described in the analysis of clays (p. 605); about 15 or 20 grains of the residue are fused with carbonate of potassa and soda.

Determination of Alkalies.—About 15 or 20 grains of the residue are ignited with three or four parts of hydrate of baryta, and the alkalies estimated as in the analysis of glass (p. 624).

The results of the analysis of the insoluble residue are also calculated upon 100 parts of the air-dried soil.

In calculating the results of the analysis of a soil, the constituents of the aqueous solution should be arranged upon the same principles as in the analysis of waters.

The whole of the lime and magnesia in the portion soluble in hydrochloric acid will exist as carbonates, unless sulphuric acid be present, when it will exist as sulphate of lime. The determinations of the carbonic acid, and of lime and magnesia, will therefore usually check each other.

If there be an excess of carbonic acid, it must exist as carbonate of iron or manganese. Unless good reason is seen for a different assumption, the iron and manganese are calculated as sesquioxide and binoxide, respectively.

There are evidently several means of control in the analysis of a soil.

The amount of the constituents soluble in water, found by direct determination, should agree with that determined by weighing the residue, and with the joint amount of the various substances estimated in the solution.

The sum of the weights of the substances determined in the hydrochloric solution (*plus* the carbonic acid) should coincide (or nearly so) with the amount ascertained to be soluble in the acid.

In this calculation, it must not be forgotten that the organic matter has been destroyed before dissolving the residue in hydrochloric acid, so that its weight must be added in with the substances determined in the solution.

Other methods of control will readily suggest themselves to the analyst.

ANALYSIS OF THE ASHES OF VEGETABLE SUBSTANCES.

§ 443. It would be very desirable to ascertain the exact forms of combination in which the mineral constituents exist in vegetable tissues, but, up to the present time, it has not been found possible to determine these without previously destroying the organic matters with which they are associated; and since we can never be sure that the processes employed for this purpose do not modify or decompose the saline combinations, the information thus acquired can only possess a certain relative value, enabling us to compare, with considerable accuracy, the mineral ingredients of plants with those of other plants, or of soils, but not to be regarded in the light of an actual account of the constitution of the mineral portion of the plant.

Much attention has been bestowed by analytical chemists upon the preparation of the ashes of vegetable substances for analysis, so that they may suffer the least possible alteration, but nearly every method which has at present been used for this purpose, is based upon the destruction of the organic matter by heat.

When we remember that vegetable tissues generally contain compounds of the alkalis and alkaline earths with organic acids, together with silicic acid, sulphates, phosphates, and chlorides, and that, in the destruction of the organic matter by heat, these substances are exposed to a high temperature in contact with charcoal and moisture, we are not surprised that a considerable alteration should be effected in these constituents by the incineration.

Since the old method of preparing the ashes of vegetables is by far the simplest and most easy of execution, and has not yet been fairly superseded by any other which lays claim to very superior accuracy, we shall here consider the analysis of ashes prepared by that method, merely suggesting, that if all analyses were carefully executed by one standard method, the purposes of comparison would be fully answered.

INCINERATION OF VEGETABLE SUBSTANCES.

The portion of the plant intended for incineration must be thoroughly cleansed with a dry cloth.

Roots and woods may be cut up into slices or fragments, and dried in an oven. Fruits are also cut into slices and dried in the same way. Seeds, leaves, and flowers are simply dried. [Stalks, straw, &c. may be conveniently dried, laid in bunches, and kindled at a flame, the ash being allowed to fall into a dish, and the incineration subsequently completed in the ordinary way. Or, the stalks, &c. may be cut into small pieces and incinerated.]

The substance, thus prepared, is placed in an earthen crucible, or in a porcelain dish, and gradually heated over a charcoal fire. As soon as the matter is thoroughly carbonized, and no more fumes are evolved, the heat is somewhat raised, and continued for a considerable period (several hours are sometimes necessary), until all or the greater part of the carbon has burnt off; the heat must not be sufficient to fuse the ash.

If a large quantity of carbon still remains unburnt, the incineration is carried further in a platinum capsule, over a gas-burner, the ashes being stirred at intervals, with a platinum spatula.

When all or the greater part of the carbon is consumed, so that the ashes appear white or light gray, a small specimen is taken out and treated with hydrochloric acid; if any hydrosulphuric acid is evolved, the ash must be mixed (in a mortar) with a small quantity of pure red oxide of mercury (which volatilizes without residue) and heated in the platinum dish (covered) until all the oxide is volatilized. (A portion of the ash is boiled with dilute nitric acid, filtered, and tested with hydrosulphuric acid.) In this way, any sulphide, arising from the reduction of the sulphates by the charcoal, is oxidized and reconverted into sulphate.

The ash is well mixed and preserved in a stoppered bottle.

Determination of the total amount of Ash.—A quantity of the vegetable substance varying with the amount of ash which it is likely to yield, is dried in the water-oven until its weight is constant. It is then very carefully incinerated in a platinum crucible, till nearly the whole of the carbon has burnt off. A quantity of pure red oxide of mercury is then mixed with the ash in the crucible, and the mixture very strongly ignited. The ash is afterwards moistened with carbonate of ammonia, thoroughly dried in an air-bath, and weighed.

In very accurate determinations, these operations should be repeated until the weight is constant.

QUALITATIVE ANALYSIS.

The following constituents are usually found in the ashes of plants:—

<i>Bases.</i>	<i>Acids.</i>
Potassa	Sulphuric
Soda	Phosphoric
Lime	Hydrochloric
Magnesia	Silicic
Alumina	Carbonic.
Protosquioxide of manganese	
Sesquioxide of iron.	

In marine plants, also, bromine and iodine should be sought.

Fluorine is occasionally found in ashes of plants.

The ashes also usually contain more or less unconsumed carbon, and some sand mechanically adhering to the plant.

A portion of the ash is boiled with water, and filtered.

The aqueous solution is tested in the usual manner, for the bases and acids mentioned above.

The residue insoluble in water is washed and boiled with dilute hydrochloric acid.

Effervescence of course indicates carbonic acid, which should not be accompanied by hydrosulphuric acid, if the preparation of the ash has been properly effected.

The acid solution is examined, as usual, for the above bases and acids (except carbonic and hydrochloric).

The portion insoluble in hydrochloric acid (which most frequently consists of sand mechanically adhering to the plant, and of unconsumed carbon), is washed, dried, ignited, if necessary, to burn off the carbon, and, should it be deemed requisite, analyzed, as usual, by Table VIII.

It is only, however, in the case of ashes very rich in silicic acid (*equisetaceæ*, &c.) that it is necessary to examine this residue.

QUANTITATIVE ANALYSIS.

It is rarely necessary, except for some special purpose, to analyze the aqueous solution separately.

Determination of Carbonic Acid.—About 30 or 40 grains of ash are employed for the estimation of the carbonic acid according to the method of Fresenius and Will (p. 617).

Determination of Chlorine.—15 or 20 grains of the ash are boiled in a flask, with dilute nitric acid (the acid being gradually added to water previously poured over the ash), and the chlorine determined, in the filtered solution, as chloride of silver.

Determination of the Remaining Constituents. (The manganese and alumina are very rarely determined in ashes).—About 100 grs. of ash are introduced into a flask, covered with water, and hydrochloric acid gradually added in considerable excess. The contents of the flask are then boiled for some time, thoroughly rinsed out into a porcelain dish, and evaporated to dryness in the air-bath. The residue is treated, as usual, with dilute hydrochloric acid, the insoluble portion (silicic acid, sand, and charcoal) collected on a weighed filter containing very little ash, washed till the washings have no acid reaction, and dried.

The acid filtrate and washings are evaporated to a small bulk, and accurately weighed in a stoppered bottle.

Determination of Sulphuric Acid.—About $\frac{1}{4}$ of the solution is employed for the determination of sulphuric acid as sulphate of baryta.

Determination of Alkalies.—In $\frac{1}{2}$ of the solution, the alkalies are determined, just as in the analysis of the hydrochloric solution of a soil.

Determination of Phosphoric Acid, Lime, Magnesia, and Sesquioxide of Iron.—The remaining $\frac{1}{2}$ of the solution (which should be mixed with more free hydrochloric acid) is treated with a slight excess of acetate of potassa; if this reagent should produce a pink color, indicating an excess of sesquioxide of iron, the solution is boiled, filtered, and the phosphoric acid and iron determined as in the analysis of soils; the lime and magnesia are subsequently determined in the filtrate.

If, however, the acetate of potassa produces merely a yellowish-white precipitate, this is filtered off, washed, dried, ignited, and weighed as phosphate of sesquioxide of iron ($2\text{Fe}_2\text{O}_3 \cdot 3\text{PO}_5$).

The remainder of the phosphoric acid is then separated from the filtrate, by adding sesquichloride of iron till a pink color is produced, boiling, and determining the phosphoric acid in the precipitate as at p. 593.

The lime and magnesia are then determined in the filtrate as usual.

Examination of the residue of Silica, Sand, and Charcoal.—If this residue consists, as is generally the case, of the above substances only, it is (after drying at 212°F . and weighing) transferred from the filter (which is afterwards again weighed, to ascertain how much of the residue has been employed) to a platinum dish, and boiled with a dilute solution of potassa (free from alumina) for about 30 minutes, when the silica is entirely dissolved. The residue of sand and charcoal is collected upon a weighed filter, well washed, dried at 212°F ., and weighed. The filter is then incinerated as usual, and the weight of the sand deducted from that of the sand and charcoal, in order to obtain the amount of the latter.

To find the quantity of silica, the weight of the sand and charcoal must be deducted from that of the original residue. But if qualitative analysis has shown that other constituents are to be determined in the residue left by hydrochloric acid, the process must be somewhat modified.

About 50 or 60 grains of the residue are heated with solution of pure potassa or soda, in a platinum or silver dish. The mixture is afterwards evaporated to dryness, the residue carefully dissolved in an excess of hydrochloric acid, and again evaporated to dryness. The subsequent process is then conducted exactly as in the analysis of the hydrochloric solution of the ash, except as regards the determination of alkalies.

This must be effected in another portion of the ash or residue, by heating with hydrate of baryta, as in the analysis of glass (p. 624).

In calculating and stating the results of an analysis of a vegetable ash, it must be remembered that the carbonic acid, sand, and charcoal are not essentially constituents of the mineral portion of the plant, but may be said to be derived from extraneous sources. These should therefore be subtracted from the ash employed, and the other ingredients calculated for 100 parts of ash, free from these impurities.

The chlorine should be calculated as chloride of sodium, and if there be an excess, as chloride of potassium. Any excess of sodium or potassium must be stated as soda or potassa.

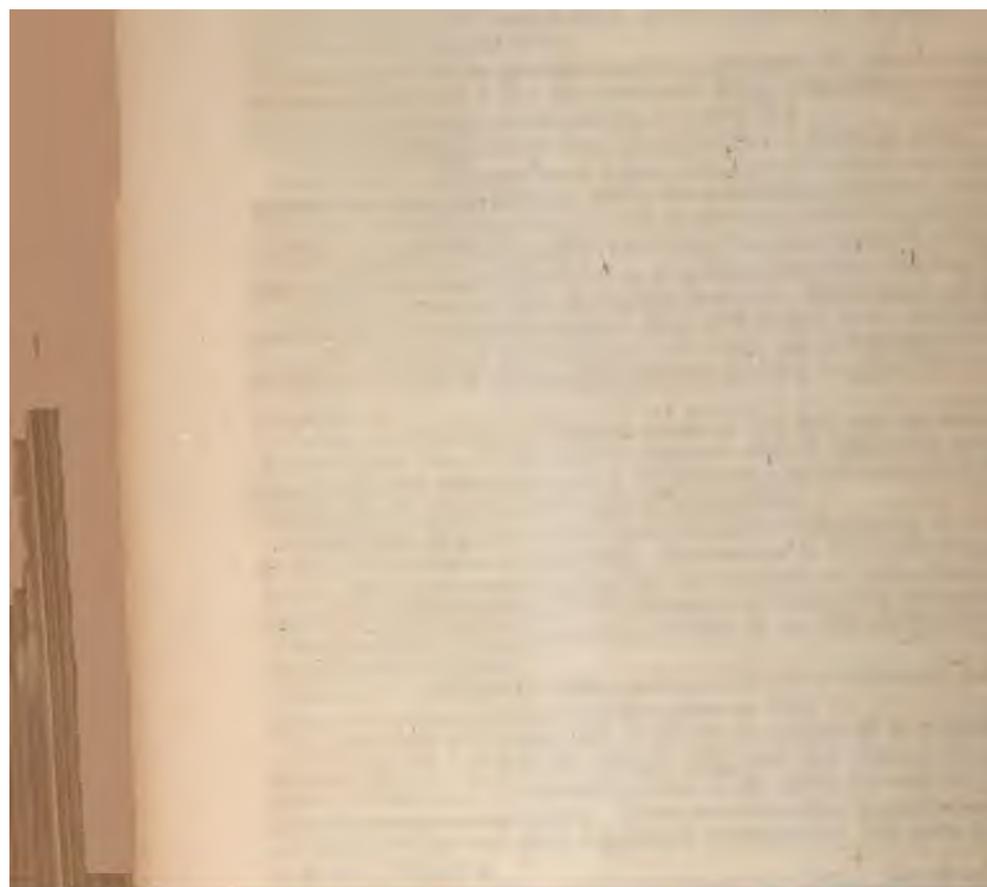
It is also usual to calculate the total amount of oxygen contained in the bases present.

ANALYSIS OF THE ASHES OF ANIMAL SUBSTANCES.

§ 444. The above method will serve, with some modifications, for the analysis of animal ashes. Since these, however, are generally free from sand, it is unnecessary to digest the silica with potassa.

It is advisable, also, in the analysis of animal ashes, to determine the amount dissolved by water, and to analyze the aqueous solution separately.

In these ashes, there is always more phosphoric acid than corresponds to the iron present. It will, therefore, be necessary to adopt the second of the methods given in the analysis of ashes, for the determination of phosphoric acid and iron.



INDEX.

- ABSORBING BALLS, 74**
Acetic acid, examination, 501
 reactions, 546
Acid, antimonioic, 430
 antimonious, 431
 arsenic, 440
 arsenious, 438
 auric, 396
 bismuthic, 392
 boracic, 215
 carbonic, 197
 solvent action, 199
 chloric, 139
 chlorocarbonic, 197
 chlorochloric, 140
 chlorochromic, 334
 chloronitric, 143
 chloronitrous, 143
 chloroperchloric, 141
 chlorosulphuric, 276
 chlorous, 139
 chromic, 330
 common phosphoric, 178
 croconic, 197
 cupric, 383
 definition, 40
 dimetaphosphoric, 178
 dithionic, 158
 ferric, 344
 fluoboric, 217
 glacial phosphoric, 177
 hexametaphosphoric,
 178
 hydriodic, 150
 hydriodous, 150
 hydrobromic, 146
 hydrochloric, 142
 hydrofluoboric, 217
 hydrofluoric, 153
 hydrofluosilicic, 227
 hydroselenic, 171
 hydrosulphuric, 165
 hydrosulphurous, 165
 hydrotelluric, 450
 hypochloric, 139
 hypochloronitric, 143
 hypochlorous, 137
 hyponitric, 127
 hyponitrous, 126
 hypophosphoric, 176
 hypophosphorous, 175
- Acid, hyposulphuric, 158**
 hyposulphurous, 156
 iodic, 149
 manganic, 359
 metantimonioic, 431
 metaphosphoric, 177
 metastannic, 423
 molybdic, 447
 monometaphosphoric,
 177
 muriatic, 142
 of commerce, 142
 niobic, 493
 nitric, 127
 nitromuriatic, 143
 nitrosulphuric, 166
 nitrous, 126
 commercial, 180
 osmic, 416
 osmious, 416
 pelopic, 494
 pentathionic, 164
 perchloric, 141
 perchromic, 333
 periodic, 150
 permanganic, 350
 phosphatic, 176
 phosphoric, 176
 phosphorous, 176
 pyrophosphoric, 178
 rhodizonic, 197
 ruthenic, 418
 selenic, 170
 selenious, 170
 silicic, 219
 stannic, 423
 sulphantimonioic, 435
 sulpharsenic, 442
 sulpharsenious, 442
 sulphocarbonic, 212
 sulphotungstic, 446
 sulphuric, 159
 distillation, 161
 sulphurous, 157
 tantalioic, 493
 telluric, 449
 tellurous, 449
 tetrametaphosphoric,
 178
 tetrathionic, 164
 titanioic, 451
- Acid, tribasic phosphoric, 173**
 trimetaphosphoric, 173
 trithionic, 164
 tungstic, 445
 vanadic, 374
Acidimetry, 619
Acids, general examination
 for, 560
 inorganic, analytical
 classification, 532
 mono-, bi-, and tri-basic,
 40
 organic, analytical, clas-
 sification, 542
 preliminary examination
 for, 559
 special tests for, 564
- Adapters, 78**
Adularia, 316
Aeroliths, 349
Elite, 349
Affinity, 43
After-damp, 202
Agate, 219
 Agate mortar, 106
 Air, analysis of, 130
 Air, atmospheric, 130
 Air-baths, 95, 570, 571
Alabaster, 296
Albite, 256
Albite, potash-, 317
 Alcohol-potash, 232
Alkali, definition, 40
 Alkalies, determination in
 silicates, 623
Alkalimetry, 616
Allouphane, 316
 Allotropy, 155
 Alloy, defined, 229
 Alloy for musical instru-
 ments, 387
Alloys, division of, 84
 of antimony, 436
 bismuth, 393
 copper and tin, 387
 copper and zinc, 387
 gold, 400
 lead, 481
 platinum, 410
 silver and copper, 492
 tin, 427

- Alloys, qualitative analysis, 567
- Alum, 818
 ammonia-, 816
 analysis, 604
 burnt, 815
 chrome-, 829
 cubical, 815
 manganese- (natural), 857
 Roman, 818
Alum-shale, 318
Alum-slate, 318
 Alum, soda-, 816
Alum-stone, 318
 Alum, uses, 816
Alumen ustum, 815
 Alumina, 810
 basic sulphate, 812
 carbonate, 816
 determination, 585
 hydrates, 811
 Alumina-mordant, 812
 Alumina, nitrate, 812
 phosphate, 816
 Alumina-potash-alum, 813
 Alumina, reactions, 518
 silicates, 816
 sulphate, 812
 Aluminate of magnesia, 812
 potassa, 812
Aluminite, 812
 Aluminum, 810
 and sulphur, 821
 sesquichloride, 821
 Alums, 812
 Amalgamated zinc, 465
 Amalgamation-process, 399
 Amalgam, defined, 229
 Amalgams, 465
 qualitative analysis, 567
 Amalgam, quantitative analysis, 612
Amethyst, 810
Amianth, 308
 Amides, formation, 276
 Amidide of potassium, 182
 Amidogen, 182
 Ammonia, 183
 Ammonia-alum, 816
 Ammonia, antimoniate, 431
 bicarbonate, 278
 bichromate, 333
 bimetantimoniate, 432
 bisulphate, 277
 bisulphite, 276
 carbonate, 278
 determination, 592
 examination, 503
 hydrosulphate, 280
 metantimoniate, 432
 muriate, 278
 nitrate, 276
 nitrite, 275
 phosphates, 277
 preparation, 183
- Ammonia, reactions, 511
 sesquicarbonate, 277
 examination, 508
 solid, 188
 solution, 184
 sulphate, 276
 sulphite, 276
Ammoniz aqua fortissima, 184
 Ammonium, 184, 275
 Ammonium-amalgam, 185, 275
 Ammonium, aurochloride, 898
 bisulphide, 280
 bromide, 280
 chloride, 278
 examination, 508
 hydrosulphate of sulphide, 280
 iodide, 280
 oxide, 275
 sulphide, 280
 examination, 508
 theory, 185
 Amorphous bodies, 51
Amphibole, 306
Analcime, 256
 Analyses, calculation, 600
 Analysis, definition, 495, 496
 for acids, Tables VI. and VII., 562, 568
 for bases, Tables I. to V. 551-555
 of air, 180
 alloys, 567
 amalgams, 567, 612
 animal ashes, 642
 alum, 604
 brass, 611
 Britannia-metal, 611
 bronze, 611
 calamine, 608
 cast-iron, 624
 chloride of sodium, 600
 chrome-iron ore, 604
 clays, 605
 coal, 188
 coal-gas, 205
 copper-pyrites, 608
 crystallized sulphate of copper, 608
 fusible alloy, 610
 German silver, 611
 glass, 621
 gun-metal, 611
 gunpowder, 619
 heavy-spar, 601
 insoluble silicates, 621
 insoluble substances, 567
 iron ores, 606
 lead-glass, 624
 limestones, 602
 manganiferous spathic iron-ore, 608
 marble, 602
- Analysis of mineral waters, 628
 pewter, 609
 platinum-ores, 418
 quartz, 594
 Rochelle salt, 602
 Seignette salt, 602
 silver-ores, 498
 soils, 635
 speiss-cobalt, 612
 standard gold, 612
 silver, 612
 sulphate of baryta, 601
 tartar-emetie, 609
 tartrate of potassium soda, 602
 type-metal, 610
 ultramarine, 626
 vegetable ashes, 640
 waters, 628
 wavellite, 606
 operations in, 571
 preparation of substances for, 546
 proximate, 495
 of coal, 190
 qualitative, apparatus for, 497
 quantitative, apparatus for, 570
 reagents for, 499
 systematic, 546
 ultimate, 495
Anatase, 450
Andalusite, 816
Anhydrite, 296
 Anhydrous, 69
 Animal charcoal, 193
 purification of, 195
 Annealing, 223
Anorthite, 811
Anthosiderite, 344
Anthracite, 187
 Antichlore, 259
Antimonial silver, 490
 Antimoniate of ammonia, 431
 potassa, 431
 teroxide of antimony 431
 Antimonic acid, 430
 determination, 583
 reactions, 525
 Antimonious acid, 431
 Antimoniuretted hydrogen 432
 Antimony, 428
 alloys, 436
 antimoniate of teroxid 431
 basic nitrate, 430
 butter, 433
 chlorosulphide, 434
 determination in alloy: 588
 flowers, 430
 glass, 435

- Antimony, golden sulphuret,** 486
 liver, 435
Antimony, 430
Antimony, metallurgy, 436
 native, 486
Antimony-ochre, 486
Antimony-ore, gray, 434
 red, 434
 white, 429
Antimony-ores, assay, 437
Antimony, pentachloride, 438
 pentasulphide, 435
 pharmaceutical preparations, 437
 purification, 428
 regulus, 428
 sesquichloride, 433
 sesquioxide, 429
 suboxide, 429
 sulphates, 430
 terbromide, 434
 terchloride, 433
 terfluoride, 434
 teriodide, 434
 teroxide, 429
 determination, 583
 reactions, 524
 tersulphide, 434
Apatite, 298
Apparatus for qualitative analysis, 497
Aqua-fortis, 130
Aqua regia, 143
Aqueous fusion, 56
 vapor, 121
Argand lamp, 102
Argentan, 389
Arragonite, 299
Arseniate of silver, 440
Arseniate of potassa, 440
 soda, 440
Arsenic, 437
Arsenic acid, 440
 determination, 584
 reactions, 530
Arsenic and tin, 443
Arsenical caustic, 443
Arsenical iron, 443
Arsenical pyrites, 437
Arsenic, bisulphide, 442
 chlorosulphide, 441
 octodecasulphide, 443
 pentasulphide, 442
 pharmaceutical preparations, 443
 reduction-tubes, 112
 subsulphide, 442
 terchloride, 441
 tersulphide, 442
 white, 438
 with metals, 443
Arsenide of manganese, 443
Arsenides of copper, 443
 iron, 443
Arsenite of copper, 440
 potassa, 439
Arsenious acid, 438
 determination, 584
 reactions, 525
Arseniuretted hydrogen, 441
Artificial gems, 311
Asbestos, 308
Ashes, animal, analysis, 642
 vegetable, analysis, 640
Aspirator, 96
Assay of
 alloys of gold by cupellation, 401
 antimony-ores, 437
 auriferous ores, 402
 bismuth-ores, 394
 copper-ores, 389
 galena, 432
 iron-ores, 355
 mercury-ores, 467
 silver-ores, 493
 tin-ores, 429
 zinc-ores, 366
Atacamite, 384
Atmospheric air, 130
Atomic theory, 42
 weights, 41
Augite, 308
Aurate of potassa, 396
 soda, 396
Auric acid, 396
Auriferous ores, assay of, 402
 valuation of, 402
Auriferous sand, examination by washing, 402
Aurosulphite of potassa, 396
Aurum musivum, 426
Aurum potable, 397
Axes of crystals, 52

BALANCES, 571
Balling process, 265
Barilla, 263
Bar-iron, 353
Barium, 282
 binoxide, 285
 chloride, 286
 examination, 503
 fluoride, 286
 hydrosulphate of sulphide of, 287
 pentasulphide, 287
 silicofluoride, 287
 sulphide, 287
 tersulphide, 287
Baryta, 282
 biborate, 285
 bicarbonate, 285
 bisulphate, 284
 borate, 285
 carbonate, 285
 chlorate, 283
 determination, 588
 hydrate, 283
Baryta, hyposulphite, 287
 nitrate, 283
 permanganate, 361
 phosphate, 284
 reactions, 511
 seleniate, 284
 sesquicarbonate, 285
 sulphate, 284
 sulphite, 284
Baryta-water, 283
Basalt, 317
Base, definition, 40
Bases, preliminary examination for, 547
Basic salts, 49
 water, 56
Bathgate coal, 186
Baumé's flux, 237
Beakers, 87
Bell-metal, 389
Benzoic acid, reactions, 545
Berlin porcelain, 320
Beryl, 321
Beryllium, 320
Berzelius's lamp, 102
Bibasic acid, definition, 40
Biborate of soda, 269
Bicarburetted hydrogen, 207
 of Faraday, 208
Bimetantimoniate of ammonia, 432
 potassa, 432
 soda, 432
Binary theory of acids, 163
Bismuth, 390
Bismuth-amalgam, 466
Bismuth arsenide, 392
 bisulphide, 392
Bismuth-blende, 392
Bismuth, carbonate, 392
Bismuth-glance, 392
Bismuthic acid, 392
Bismuth, metallurgy, 393
Bismuth-minerals, 393
Bismuth, nitrate, 391
Bismuth-ochre, 393
Bismuth-ores, assay, 394
Bismuth, oxychloride, 391
 suboxide, 391
 sulphate, 392
 terchloride, 391
 teroxide, 391
 determination, 579
 reactions, 520
 tersulphide, 392
 trisnitrate, 391
Bismuthum album, 391
Bismuth, uses, 393
Black ash, 265
Black-band, 350
Black flux, 99
Black-jack, 366
Black-lead, 185
Black's blowpipe, 105
Black's furnace, 104
Blanquette, 263

- Blast-furnace, 350**
Bleaching, 295
Bleaching-compounds, 188
Bleaching liquid of Labarraque, 258
Bleaching powder, 294
 valuation, 616
Bleaching power of chlorine, 186
Block-tin, 427
Blood-stone, 849
Blowpipe-flame, 107
Blowpipe-flames, colored, 110
Blowpipe-lamp, 106
Blowpipe-reagents, 106
Blowpipe-supports, 106
Blowpipe, use of, 105
Blue copper, 385
 copperas, 380
 malachite, 382
 stone, 380
 verditer, 380
 vitriol, 380
 vitriol of commerce, examination of, 381
Boiler-incrustations, 381
Boiling-points, determination of, 82
Bola, 318
Bologna phosphorus, 287
Bone-ash, 298
Bone-black, 198
Bone-earth, 298
 as manure, 298
Boracic acid, 215
 determination, 598
 manufacture, 215
 reactions, 584
Borate of
 magnesia and soda, 308
 soda, 269
Borates, 216
 of baryta, 285
Borax, 269
 for blowpipe reagent, 107
 octohedral, 269
 manufacture, 269
 uses, 270
 vitrified, 270
Borofluoride of potassium, 215
Boron, 214
 and nitrogen, 217
 and sulphur, 217
 terchloride, 217
 terfluoride, 217
Braunite, 358
Bricks, refractory, 319
Brass, 387
 analysis, 691
Britannia metal, 427
 analysis, 611
Brittle silver ore, 490
Brochantite, 382
Bromate of potassa, 249
Bromates, 146
Bromic acid, 146
Bromide of ammonium, 280
 antimony, 484
 lead, 470
 potassium, 252
 silicon, 227
 silver, 489
 sodium, 278
 sulphur, 168
Bromides, 147
Bromides of
 iodine, 152
 iron, 346
 mercury, 468
 phosphorus, 188
 selenium, 171
 sulphur, 168
Bromine, 145
 action of, upon organic substances, 152
 chloride, 147
 determination, 597
 and silica, 227
 hydrate, 146
Bronze, 388
 analysis, 611
Bronze-powder, 426
Brookite, 450
Brown coal, 186
Brown iron-ore, compact, 342
 fibrous, 342
Brucite, 304
Brunner's method of analyzing silicates, 628
Brunswick green, 384
Bude-light, 116
Bulb absorption-tubes, 74
Bulb-tubes, 112
Butter of antimony, 493
 zinc, 365
CADMIUM, 376
 carbonate, 377
 chloride, 377
 nitrate, 377
 oxide, 376
 determination, 580
 reactions, 521
 subsulphate, 377
 sulphate, 377
 sulphide, 377
Caking coal, 187
Calamine, 364
 analysis, 608
 electric, 365
Calcareous spar, 299
Calcium, 289
 binoxide, 300
 bisulphide, 302
Calcium, chloride, 301
 examination, 504
Calcium, fluoride, 301
 oxychloride, 301
 oxysulphide, 302
 pentasulphide, 302
 phosphide, 303
Calcium, sulphide, 302
Calomel, 459
Cannel coal, 186
Canton's phosphorus, 302
Caoutchouc joints, 65
Capillary pyrites, 369
Carbamide, 276
Carbides, 214
Carbon, 184
Carbonate of
 alumina, 816
 baryta, 285
 bismuth, 392
 cadmium, 377
 glucina, 322
 iron, 342
 lime, 299
 lime and soda, 300
 lithia, 275
 manganese, 357
 potassa and soda, 268
 sesquioxide of chromium, 330
 silver, 487
 strontia, 288
 zinc, 364
Carbonates, 200
 of ammonia, 277
 cobalt, 371
 copper, 382
 lead, 473
 magnesia, 307
 mercury, 458
 potassa, 250
 soda, 263
Carbon-batteries, 194
Carbon, bisulphide, 212
 chlorides, 210
 general properties of, 193
Carbonic acid, 197
 composition, 199
 determination, 596
 liquefaction, 75
 liquid, 198
 reactions, 536
 solid, 198
 solidification, 76
 solvent action, 199
Carbonic oxide, 195
Carbonic oxide series, 197
 test for, 197
Carbon, perchloride, 212
 protochloride, 212
 sesquichloride, 212
 uses, 194
Carburets, 194
Cast-iron, 352
 analysis, 624
 black, 353
 gray, 353
 impurities in, 352
 white, 353
Catalysis, 47
Caustic potassa, 232
 soda, 257

- Caustic soda, preparation for soap-boiling, 257**
Celestine, 288
Cement, limestone for, examination, 292
 Portland, 292
 Ransome's vitrified, 298
 Roman, 292
Cementation process, 354
Cerite, 324
Cerium, 324
 oxide, 325
 reactions, 325
 salts, 325
 sesquioxide, 325
Ceruse, 473
Chalcedony, 219
Chalcolite, 335
Chalk, precipitated, 299
Chameleon-mineral, 359
Charbon-roux, 192, 243
Charcoal, 190
 absorption of gases by, 192
 burning, 190
 deoxidizing properties of, 194
 for fuel, 104
 properties of, 192
Charcoal supports, 106
Charring by steam, 192
Chaufer, 104
Chemistry, definition of, 33
Chili-saltpetre, 257
China, 320
China, glazing, 320
Chlorate of
 baryta, 238
 potassa, 247
 soda, 258
Chlorates, 140
 uses, 140
Chloric acid, 139
 determination, 599
 reactions, 542
Chloride of
 aluminum, 321
 ammonium, 278
 arsenic, 441
 barium, 286
 boron, 217
 bromine, 147
 cadmium, 377
 cerium, 325
 glucium, 322
 lime, valuation, 616
 magnesium, 309
 nickel, 369
 nitrogen, 144
 potassium, 251
 silicon, 226
 silver, 487
 soda, 258
 sodium, 271
 strontium, 288
Chloride of tantalum, 493
 uranyle, 337
 vanadium, 374
 yttrium, 324
 zirconium, 326
Chlorides, 144
Chlorides of
 antimony, 433
 bismuth, 391
 calcium, 301
 carbon, 210
 chromium, 333
 cobalt, 372
 copper, 388
 gold, 397
 iodine, 152
 iridium, 415
 iron, 345
 lead, 477
 lithium, 275
 manganese, 361
 mercury, 459
 molybdenum, 448
 niobium, 498
 osmium, 417
 palladium, 412
 phosphorus, 181
 platinum, 407
 rhodium, 418
 ruthenium, 418
 selenium, 171
 sulphur, 167
 tellurium, 450
 tin, 424
 titanium, 452
 tungsten, 445
 uranium, 337
 zinc, 365
Chlorimetry, 615
Chlorine, 136
 action of, upon organic substances, 152
 determination, 597
 hydrate, 137
 peroxide, 139
Chlorine-water, 136
Chlorocarbonic acid, 197
Chlorochloric acid, 140
Chlorochromate of potassa, 333
Chlorochromic acid, 334
Chloronitric acid, 143
Chloronitrous acid, 143
Chloroperchloric acid, 141
Chlorophosphide of nitrogen, 183
Chlorostannates, 425
Chlorosulphide of nitrogen, 167
Chlorosulphide of phosphorus, 182
 silicon, 228
Chlorosulphuric acid, 277
Chlorous acid, 139
Chromate of
 ammonia, 333
Chromate of soda, 333
 suboxide of mercury, 456
Chromates, 331
 of lead, 475
 potassa, 331
 sesquioxide of chromium, 338
Chrome-alum, 329
Chrome-iron ore, 327
 analysis, 604
Chrome-yellow, 475
Chromic acid, 330
 determination, 595
 reactions, 535
Chromium, 326
 brown oxide, 327
 chloride, 333
 fluoride, 335
 nitride, 333
 oxide, 327
 oxychloride, 334
 protosesequioxide, 330
 sesquichloride, 334
 sesquioxide, 327
 carbonate, 330
 chromate, 333
 determination, 585
 nitrate, 329
 reactions, 514
 sulphate, 329
Chromium, sulphides, 335
Chrysocola, 333
Chrysolite, 308
Cinders, 187
Cinnabar, 464
 valuation, 577
Citric acid, reactions, 544
Clark's process for softening water, 122
 soap-test, 632
Clay, fire- 318
Clay-ironstone, 349
Clay, pipe- 318
 potter's, 318
Clays, 317
 analysis, 605
 chemical characters, 318
Cleavage, 52
Coal, 185
 analysis, 188
 ash, 187
 Bathgate, 186
 black, 186
 brown, 186
 caking, 187
 cannel, 186
 cubical, 186
 decomposition, 187
 glance, 187
 peacock, 187
 pit, 187
 pitch, 186
 proximate analysis, 190
 splint, 186
 Welsh, 187
Coal-fires, 187

- Coal-gas, 203
 analysis, 205
 mines, explosions in, 203
 tar-naphtha, 205
- Cobalt, 370
 carbonates, 371
 chloride, 392
 double sulphate, 371
 nitrate, 371
 nitrate, for blowpipe reagent, 107
- Cobalt-ore, gray*, 373
white, 373
- Cobalt, oxide, 370
 oxide, determination, 587
 oxide, reactions, 516
 oxysulphide, 373
 protoxide, 370
- Cobalt-pyrites*, 373
- Cobalt, sesquichloride, 372
 sesquioxide, 371
 sesquisulphide, 373
 subarsenide, 443
 sulphate, 371
 sulphide, 373
 technical history, 373
- Cobalt, Tunaberg*, 373
- Coke, 190
 hearths, 191
- Colcothar, 341, 342
- Colors for glass, 225
- Columbium, 493
- Combination, 44
 by volume, 43
- Combining proportions, 41
- Combustion-furnace, 104
 table, 103
 tubes, 112
- Common phosphates, 179
 phosphoric acid, 178
 salt, 271
- Composition of water determined, 120
- Condensation of gases, 74
- Condensing apparatus, 80
- Condurrite*, 443
- Constitutional water, 56
- Copper, 377
- Copper-amalgam, 466
- Copper, ammoniochlorides, 384
 ammonio-nitrate, 380
 ammonio-sulphates, 382
 and silver, alloys, 466
 and tin, alloys, 387
- Copper and zinc, alloys, 387
 arsenides, 433
 arsenite, 440
- Copperas, 340
 blue, 380
- Copper-Azure*, 382
- Copper, basic nitrate, 380
 basic sulphates, 382
 bibasic carbonate, 382
 Linoxide, 333
- Copper, black oxide, 379
- Copper, blue carbonate*, 385
 carbonate, 382
 chloride, 384
 commercial, purification, 377
 determination, in ores, 580
 double carbonates, 382
 double sulphates, 381
 engraving on, 387
- Copper-glance*, 384
- Copper, hydrated oxide, 380
 hydride, 383
 metallurgy, 385
- Copper-native*, 385
- Copper-nickel*, 369
- Copper, nitrate, 380
 nitride, 383
- Copper-ore, gray*, 386
red, 378
variegated, 386
- Copper-ores, assay, 389
- Copper, oxide, 379
 determination, 579
 reactions, 520
 oxychlorides, 384
 oxysulphide, 385
 phosphides, 385
- Copper-pyrites*, 385
 analysis, 608
- Copper, red oxide, 378
 silicates, 383
 subchloride, 383
 suboxide, 378
 subsulphate, 379
 subsulphide, 384
 sulphate, 380
 analysis, 608
 uses, 381
 sulphide, 385
 tinning, 389, 427
 uses, 387
- Coquimbite*, 343
- Cork-borers, 61, 497
- Corks, 60
 perforation of, 61
- Correction of gases for pressure, 38
- Correction of gases for temperature, 38
- Corrosive sublimate, 460
- Corundum*, 310
- Croconic acid, 197
- Crocus, 435
- Crucible-jacket, 98
- Crucibles, 100
 composition, 310
 lined with charcoal for iron reductions, 100
 precautions in heating, 98
- Crushing, 84
- Crushing mortar, 8
- Crystals, feeding, 97
 forms of, 52
- Crystals from the leaden chambers, 160
- Crystallization, 51, 96
 by fusion, 97
 by solution, 96
 by vaporization, 97
 promoted, 97
 purification by, 96
 water of, 56
- Crystallography, 52
- Cubical coal, 186
- Cubic nitre, 257
- Cupel, 480
- Cupellation, 480
- Cupric acid, 383
- Cyanite*, 316
- Cyanogen, 209
 compounds, 210
 liquefaction of, 209
- Cylinder-charcoal, 192
- DECANTATION, 92
- Decantation, washing by, 93
- Decoction, 90
- Decomposition, 46
- Decrepitation, 107
- Definition of chemical terms, 40
- Deflagration, 107
- Deflagrating-spoons, 71
- Deliquescence, 95
- Derbyshire spar*, 302
- Desiccating tubes, 66
- Desiccation, 95
in vacuo, 94
 of volatile bodies, 96
- Desiccators, 95
- Destructive distillation, 46
- Determination of
 alkalies in silicates, 623
 alumina, 685
 ammonia, 592
 antimonic acid, 683
 antimony in alloys, 683
 arsenic acid, 684
 arsenious acid, 684
 baryta, 588
 binoxide of platinum, 681
 tin, 682
 boracic acid, 593
 bromine, 597
 carbonic acid, 596
 chloric acid, 599
 chlorine, 597
 chromic acid, 595
 copper in ores, 680
 fluorine, 595
 hydriodic acid, 597
 hydrobromic acid, 597
 hydrochloric acid, 597
 hydrofluoric acid, 595
 hydrosulphuric acid, 598
 iodine, 597
 lime, 590
 magnesia, 590

- Determination of**
 nitric acid, 599, 619
 oxalic acid, 596
 oxide of cadmium, 680
 cobalt, 587
 copper, 579
 lead, 578
 manganese, 588
 mercury, 577
 nickel, 587
 silver, 576
 tin, 582
 zinc, 588
 phosphoric acid, 598
 potassa, 590
 protoxide of iron, 586
 sesquioxide of chromium, 585
 iron, 585
 silicic acid, 594
 silver by standard solution, 612
 soda, 591
 stannic acid, 582
 strength of commercial acids, 619
 strontia, 589
 suboxide of mercury, 576
 sulphur, 598
 sulphuric acid, 592
 sulphurous acid, 595
 teroxide of antimony, 688
 bismuth, 579
 gold, 681
 value of commercial potash, 616
 commercial soda, 618
 manganese ore, 614
 water of constitution, 601
 crystallization, 601
Detonation, 107
Devitrification, 223
Diamond, 184
Diamond, amorphous, 185
Diaspore, 811
Didymium, 224
 reactions, 325
Diffusion of gases, 57
Diffusion-tube, 57
Digestion, 88
Dimetaphosphoric acid, 178
Dimorphous bodies, 51
Diopase, 383
Diplatosamine, 407
Diplatosammonium, 407
Dishes, 87
Disinfectants, 295
Disintegration, 84
Displacement-apparatus, 90
Disthene, 816
Distillation, 77
 at high temperatures, 77
 at lower temperatures, 79
- Distillation, at temperatures**
 below 212° F., 82
 connecting-tubes in, 80
 dry, 77
 facilitation of, 82
 fractional, 82
 on a small scale, 80
 Distilled water, 122
 for analysis, 507
 Dithionates, 159
 Dithionic acid, 158
Dolomite, 808
 Double decomposition, 47
 Drummond light, 119
 Drying-closet, 103
 Drying-tiles, 96
 Dutch liquid, 210
 Dutch metal, 387
- EAGLE-STONE**, 349
Earthenware, common, 821
 glaze for, 820
Eau de Javelle, 249
 Edulcoration, 92
 of precipitates, 574
 Efflorescence, 56
 Elective decomposition, 47
 Electrochemical theory, 46
 Electro-gilding, 400
 Electrolysis, 46
 Electro-plating, 492
 Element, definition, 118
 Elements, classification, of 118
 table of, 114
Embolite, 489
Emerald, 821
Emerald of Limoges, 822
Emery, 811
 Enamel, 225
 English porcelain, 819
 glazing, 819
 Epsom salts, 305
 Equations, 50
 Equivalent volumes, 48
 Equivalents, 40
 table of, 114
 Erbia, 324
 salts, 324
 Erbium, 328
 Ethiops mineral, 464
 Euchlorine, 188
Euclase, 322
 Eudiometer, Ure's, 71
 Eudiometers, 71
 Eudiometry, 70
 Evaporation, 94
 at the boiling temperature, 94
 below ebullition, 94
 in quantitative analysis, 572
 in vacuo, 94
 spontaneous, 94
 to dryness, 94
- FARADAY'S gas condensing tube**, 74
Feldspar, 256, 316
 lime- 317
 lithia- 317
 potash- 316
 soda- 317
Ferrate of
 potassa, 344
 soda, 345
Ferrates, 345
Ferri sulphas exsiccatum, 341
Ferric acid, 344
Ferroso-ferric oxide, 344
Filtering-paper, 91
 examination, 498
 quantitative, 570
Filtering, precautions in, 91
Filters, 91
Filter-stands, 91
Filtration, 90
Fire-clay, 318
Fire-damp, 201
Flake-white, 391
Flame, structure of, 108
Flames, luminous, 107
Flasks, drying, 630
 for distillation, 80
 gas evolution, 59
 solution, 88
Fleitmann and Henneberg's phosphates, 179
Fleitmann's test for arsenic, 529
Flint, 219
 and steel, 330
Florence flasks, 57
Fluoboric acid, 217
Fluoride of
 aluminum, 321
 antimony, 434
 barium, 286
 boron, 217
 calcium, 301
 chromium, 335
 potassium, 253
 potassium and glucinum, 328
 silicon, 227
 silver, 489
 sodium, 273
Fluorides, 154
Fluorine, 153
Fluorine, determination, 595
Fluor-spar, 301
Flux, black, 90
 Baumé's, 287
Fluxes, 90
Fly-powder, 438
Formule, 49
Freezing mixtures, 260
French chalk, 308
Fresenius and Babo's test, 526
Fuel, patent, 188
Fuel, valuation, 188

- Fuller's earth*, 318
 Fulminating gold, 396
 platinum, 406
 silver, 485
 Fuming liquor of Libavius, 425
 Funnel-bags, 90
 Funnel, hot water, 91
 Funnel-tubes, 60
 Funnels, 91
 Furnaces, 108
 Fusible alloy, 398
 analysis, 610
 Fusion, 99
 aqueous, 56
 igneous, 56
 with nitre, 101
 precautions in, 100

Gadolinite, 324
Galena, 471
 assay, 482
 Gallic acid, reactions, 544
Garnet, 817
 Gas-bags, 67
 Gas-bladders, 67
 Gas-carbon, 190
 Gas-cylinders, 68
 Gases, apparatus for collecting, 68
 collection, 67
 collection of by displacement, 69
 combustion of, 70
 combustion in, 71
 condensation, 74
 detonation, 70
 diffusion, 57
 generation of at ordinary temperatures, 64
 measurement, 72
 preparation with the aid of heat, 59
 purification, 64
 separation by absorption, 74
 solution, 73
 transference, 72
 Gasholder, P'epy's, 66
 Gas, illuminating, from water, 207
 valuation, 204
 Gas-jars, capped, 68
 stoppered, 68
 Gas-jets, 70
 lime, 205
 Gas, olefant, 207
 used as fuel, 102
 Gauze burners, 102
Gaylussite, 300
 Gems, artificial, 216, 226, 311
 General reagents, treatment with, 550
 German silver, 389
 analysis, 611

Geysers, 220
Gibbsite, 816
 Gilding, 400
 Glacial phosphoric acid, 177
Glance-coal, 187
Glance-cobalt, 373
 Glass, 221
 analysis, 621
 Bohemian, 224
 Glassblowing, 110
 Glass, bottle-, 224
 colors for, 225
 crown, 224
 flint, 225
 materials for, 224
 paste, 225
 plate-, 224
 soluble, 222
 Glass-tubing, German, 111
 operations with, 61
 Glass, window-, 224
 Glauber's salts, 259
 Glaze for earthenware, 319
 Glazes, colored, 319
 Glazing with common salt, 273
 Glucina, 322
 carbonate, 322
 reactions, 322
 sulphates, 322
 Glucinum, 321
 and potassium, double fluoride, 323
 sesquichloride, 322
 sesquisulphide, 322
Gneiss, 317
 Goadby's solution, 461
 Gold, 394
 and soda, hyposulphite, 395
 alloys, 400
 assay by cupellation, 401
 examination by touchstone, 401
 alluvial, 398
 Gold-amalgam, 466
 Gold, double chlorides, 397
 dust, 399
 extraction, 399
 fulminating, 396
 jeweller's, 400
 Gold-leaf, 400
 Gold, metallurgy, 398
 minerals, 398
 mosaic, 426
 native, 398
 Gold-ores, fusion, 399
 Gold, oxide, 395
 parting, 401
 powder, 466
 protochloride, 397
 quartation, 399
 refining, 399
 standard, 399
 analysis, 612
 sulphides, 398

 Gold, tetrachloride, 397
 terozide, 396
 determination, 681
 reactions, 521
 washing, 399
 wire, 400
 Goniometer, 56
 Grain-tin, 427
Granite, 317
 Granulation, 86
 Graphite, 185
 Green salt of magnus, 407
 Green vitriol, 340
 manufacture of, 340
Gray antimony-ore, 434
Gray copper-ore, 386
Gray nickel-ore, 369
 Gros's platinum-base, 408
Guanite, 307
 Gun-metal, 388
 analysis, 611
 Gunpowder, 239
 analysis, 619
 composition of different varieties, 241
 manufacture, 242
 properties, 246
 white, 248
Gypsum, 296

Hair-salt, 305
 Haloid salts, definition, 40
 Hannemann's soluble mercury, 456
Hausmannite, 358
 Heating arrangements, 102
Heavy lead-ore, 476
Heavy-spar, 284
 analysis, 601
 Hemming's jet, 120
Hepar sulphuris, 255
 Herapath's blowpipe, 111
 Hexametaphosphoric acid, 178
Hisingerite, 344
Hæmatite brown, 349
 red, 349
 Homberg's phosphorus, 315
Hornblende, 308, 317
Horn-lead, 478
Horn-mercury, 467
Horn-silver, 487
 Hot blast, 351
Ilyacanth, 326
 Hydrate of
 baryta, 283
 bromine, 147
 chlorine, 136
 lime, 290
 magnesia, 304
 potassa, 232
 soda, 257
 Hydrates, 49, 121
 of phosphoric acid, 177
 silica, 219
 Hydration, water, 56

- Hydraulic mortars, 291
 of Tournay, 298
 Hydriodate of potassa, 252
 Hydriodic acid, 150
 determination, 597
 reactions, 589
 Hydriodous acid, 150
Hydroboracite, 308
 Hydrobromic acid, 146
 determination, 597
 reactions, 588
 Hydrochloric acid, 142
 determination, 597
 examination, 501
 reactions, 587
 solution, 142
 Hydrocyanic acid, reactions, 540
 Hydroferricyanic acid, reactions, 541
 Hydroferrocyanic acid, reactions, 541
 Hydrofluoric acid, 153
 determination, 595
 reactions, 586
 Hydrofluoboric acid, 217
 Hydrofluosilicic acid, 227
 Hydrogen, 118
 and platinum, 407
 and silicon, 226
 antimoniuretted, 432
 arseniuretted, 441
 bicarburetted, 207
 binoxide, 123
 light carburetted, 201
 pentasulphide, 165
 phosphides, 179
 phosphuretted, 179
 purification, 118
 seleniuretted, 171
 sulphuretted, 165
 telluretted, 450
 teroxide, 116
 Hydrometers, 35
 Hydroselenic acid, 171
 Hydrosulphate of
 ammonia, 280
 potassa, 253
 sulphide of ammonium, 280
 sulphide of barium, 287
 sulphide of sodium, 273
 Hydrosulphocyanic acid, reactions, 541
 Hydrosulphuric acid, 165
 determination, 598
 hydrate, 166
 reactions, 589
 Hydrosulphurous acid, 165
 Hydrotelluric acid, 450
 Hygrometers, 181
 Hyperoxymuriate of potassa, 247
 Hypochloric acid, 139
 Hypochlorite of
 lime, 294
 magnesia, 305
 potassa, 249
 soda, 258
 Hypochloronitric acid, 148
 Hypochlorous acid, 137
 reactions, 542
 Hyponitric acid, 127
 Hyponitrous acid, 126
 Hypophosphites, 175
 Hypophosphoric acid, 176
 Hypophosphorous acid, 175
 Hyposulphates, 159
 Hyposulphite of
 baryta, 287
 gold and soda, 395
 soda, 258
 Hyposulphites, 156
 of silver, 486
 Hyposulphuric acid, 158
 Hyposulphurous acid, 156
 Ice, 120
Iceland spar, 299
 Igneous fusion, 56
 Ignition, 93
 in quantitative analysis, 573
 in tubes, 99
 of precipitates, 575
 Ilnenium, 494
 Incandescence, 107
 Incineration in quantitative analysis, 573
 of vegetables, 640
 Incrustations, 109
 in boilers, 121
 Indian fire, 442
Indigo copper, 385
 Infusion, 88
 Ink, sympathetic, 372
 Insoluble silicates, analysis, 621
 Insoluble substances, analysis of, 566
 Intumescence, 107
 Iodate of potassa, 249
 Iodates, 149
 Iodic acid, 149
 Iodide of
 ammonium, 280
 antimony, 434
 nitrogen, 151
 potassium, 252
 silver, 489
 sodium, 273
 sulphur, 168
 Iodides, 154
 of iron, 346
 lead, 470
 mercury, 463
 phosphorus, 183
 Iodine, 148
 determination, 597
 action of, upon organic substances, 152
 Iodine, bromides, 152
 chloride, 152
 compound solution of, 252
 terchloride, 152
 Iridium, 414
 bichloride, 415
 binoxide, 414
 Iridium-black, 414
 Iridium, double chlorides, 415
 oxide, 414
 protochloride, 415
 reactions, 415
 sesquichloride, 415
 sesquioxide, 414
 terchloride, 415
 teroxide, 414
 Iron, 338
 Iron-amalgam, 465
 Iron, ammonio-chloride, 346
 ammonio-nitrate, 340
 arsenical, 448
 arsenides, 443
 bar-, 353
 bisulphide, 347
 black oxide, 344
 bromides, 346
 carbonate, 342
 cast-, 353
 analysis, 624
 cold-short, 352
Iron-glance, 349
 Iron, iodide, 346
 magnetic oxide, 344
 metallurgy, 349
 meteoric, 349
 nitrate, 340
 nitride, 345
Iron-ore, micaceous, 349
 oolitic, 349
 sparry, 350
 spathic, 350
 Iron-ores, 349
 analysis, 606
 assay, 355
 preparation, 350
 smelting, 350
 Iron, oxide, 340
 determination, 586
 reactions, 515
 passive state, 339
 peroxide, 342
 protochloride, 345
 proto-sesquioxide, 344
 protosulphate, 340
 protoxide, 340
 pure, preparation, 338
 purification, 352
 oxides of, determination of relative quantities, 587
Iron-pyrites, 347
 Iron, pyrophoric, 338
 refining, 352
 rusting, 339
Iron-sand, 349

- Iron, sesquichloride, 345
 sesqui-iodide, 346
 sesquioxide, 342
 basic sulphates, 343
 determination, 585
 hydrate, 343
 nitrate, 343
 phosphate, 344
 reactions, 516
 silicates, 344
 sulphate, 343
 sesquisulphide, 347
 specular, 349
 Iron-stone, magnetic, 349
 Iron, subphosphide, 348
 subsulphide, 346
 sulphate, 340
 uses, 341
 sulphide, 347
 sulphuret, 347
 tersulphide, 348
 tinned, 427
 titanic, 450
 with boron, 349
 carbon, 348
 silicon, 349
 wrought, 358
 Isomerism, 49
 Isomorphism, 52
 Ivory-black, 193

JASPER, 219
Jet, 187
Jeweller's gold, 400
Joints in distillation, 80

Kaolin, 317
Karstenite, 296
Kelp, 263
Kermes mineral, 435
King's yellow, 442
Kryolite, 256

LABARRAQUE'S BLEACHING LIQUOR, 258
Labrador, 256
Labradorite, 317
Lagoons, 215
Lakes, 316
Lampblack, 193
Lanarkite, 475
Lanthanium, 324
 oxide, 325
 reactions, 325
 salts, 325
Lapis lazuli, 273
 Laughing gas, 124
 Law of definite and multiple proportions, 42
 Lead, 468
 alloys, 481
 Lead-amalgam, 466
 Lead, basic carbonate, 478
 nitrates, 471
 nitrites, 471
 binoxide, 476
 Lead, bromide, 478
 carbonate, 473
 chloride, 477
 chlorosulphide, 479
 chromate, uses, 475
 corrosion, 473
 dichromate, 475
 Lead-glass, analysis, 624
Leadhillite, 475
 Lead, iodide, 479
 metallurgy, 479
 Lead-minerals, 479
 Lead, neutral chromate, 475
 nitrate, 471
 nitrite, 471
 oxide, 470
 determination, 578
 reactions, 580
 oxychlorides, 478
 oxy-iodide, 478
 peroxide, 476
 protoxide, 470
 puce oxide, 476
 pure, preparation, 468
 Lead, pyrophorus, 468
 Lead, selenide, 479
 silicates, 475
 solubility in water, 469
Lead-spar, 473
 Lead, subchromate, 475
 suboxide, 469
 sulphate, 472
 sulphide, 478
 Lead-tree, 469
 Lead, uses, 481
Lead-vitriol, 472
 Leblanc's process, 264
 Lemery's volcano, 347
Lepidolite, 274
 Levigation, 86
 in blowpipe operations, 109
 Liebig's condenser, 78
 potassa-apparatus, 74
 Light carburetted hydrogen, 201
Lignite, 186
 Lime, 289
 acid phosphate, 298
 agricultural uses, 293
 and soda, double carbonate, 300
 bicarbonate, 300
 Lime, bisulphate, 289
 Lime-bleach, 294
 Lime burning, 289
 carbonate, 299
 analysis, 590
 common phosphate, 298
 determination, 590
Lime-feldspar, 317
 Lime, hydrate, 290
 hypochlorite, 294
 Lime-kilns, 289
 Lime, milk, 291
 nitrate, 293
 Lime, reactions, 512
 silicate, as manure, 219
 Limestone, 300
 for cement, examination, 292
 Limestones, analysis, 602
 Lime, sulphate, 296
 sulphite, 295
 superphosphate, 299
 triphosphate, 298
 Lime-water, 290
Liquor fumans Boylei, 281
Liquor potassæ, 233
 Litharge, 470
 reduction, 481
 uses, 471
 Lithia, 274
 carbonate, 275
Lithia-feldspar, 317
Lithia-mica, 274
 Lithia, nitrate, 275
 phosphate, 275
 reactions, 275
 salts, 275
 sulphate, 275
 Lithium, 275
 chloride, 275
 Liver of sulphur, 255
 Lixivation, 89
Loadstone, 344
Loam, 318
 Lucifer-matches, 248
 Lunar-caustic, 485
 Luting, 63

MACERATION, 89
 Magnesia, 304
Magnesia alba, 307
 Magnesia, aluminate, 312
 and ammonia, double sulphate, 306
 phosphate, 306
 and potassa, phosphate, 307
 phosphate, 305
 and soda, borate, 308
 basic carbonate, 307
 bicarbonate, 307
 calcinata ponderosa, 304
 calcined, 304
 carbonate, 307
 common phosphate, 306
 determination, 590
 heavy carbonate, 308
 hydrate, 304
 hypochlorite, 305
 nitrate, 304
 pyrophosphate, 306, 307
 reactions, 513
 sulphate, 305
Magnesia usta, 304
Magnesite, 307
 Magnesium, 303
 chloride, 309
 sulphide, 309
Magnetic iron-

- Magnetic pyrites**, 848
Malachite, 382
Malachite, blue, 382
Manganate of potassa, 359
 soda, 360
Manganese, 355
Manganese-alum (natural), 357
Manganese-alums, 357
Manganese arsenide, 443
 binoxide, 358
 uses, 359
Manganese-blende, 361
Manganese, carbonate, 357
 chloride, 361
 double sulphides, 361
Manganese-ores, valuation, 614
Manganese, oxide, 356
 determination, 588
 reactions, 518
 oxysulphide, 361
 perchloride, 361
 peroxide, 358
 phosphate, 357
 protosesquioxide, 358
 red oxide, 358
 sesquichloride, 361
 sesquioxide, 358
 sulphate, 358
 silicates, 357
 sulphate, 356
 sulphide, 361
Manganic acid, 359
Manganiferous spathic iron-ore, analysis, 608
Manganite, 358
Marble, 299
Marble, analysis, 602
Margueritte's process, 606
Marl, 318
Marsh-gas, 202
Marsh's test, 528
Mascagnine, 276
Massicot, 470
Meadow-ore, 349
Meerschäum, 308
Melanochroite, 476
Mellon, 210
Mendipite, 478
Mercuramine, 462
Mercurial-trough, 68
Mercury, 454
 amido-subchloride, 460
 ammoniated oxide, 457
 ammoniated subchloride, 460
 basic carbonates, 458
 nitrates, 458
 subnitrates, 456
 black oxide, 456
 bromide, 468
 chloramidide, 462
 chloride, 460
 cyanide, 461
 cyanides, 461
 Mercury, expansion of; by heat, 454
 extraction from its ores, 467
 iodide, 468
 manipulations with, 69
 metallurgy, 467
 native, 467
 nitrate, 458
 nitric oxide, 457
 nitride, 459
Mercury-ores, assay, 467
Mercury-oxide, 457
 determination, 577
 reactions, 519
 oxyamidide, 457
 salts, 458
 oxybromide, 468
 oxychlorides, 462
 oxyiodide, 468
 pharmaceutical preparations, 467
 protonitrate, 456
 red oxide, 457
 soluble, Hannemann's, 456
 subbromide, 468
 subchloride, 459
 subchromate, 456
 subiodide, 468
 subnitrate, 456
 suboxide, 456
 determination, 576
 reactions, 580
 subsulphate, 456
 subsulphide, 464
 sulphate, 458
 sulphide, 464
 double compounds, 465
Metal, definition, 113
Metallic powders, preparation, 86
Metalloid defined, 113
Metallurgy of
 antimony, 486
 bismuth, 398
 copper, 385
 gold, 398
 iron, 349
 lead, 479
 mercury, 467
 nickel, 369
 platinum, 410
 silver, 490
 tin, 426
 zinc, 366
Metals, analytical classification, 507
 physical properties, 494
Metantimoniate of ammonia, 482
 potassa, 481
Metantimonio acid, 481
Metaphosphate of soda, 262
Metaphosphates, 177
Metaphosphoric acid, 177
Metastannate of oxide of tin, 424
 potassa, 424
 soda, 424
Metastannic acid, 423
Meteoritic iron, 349
 stones, 349
Miasmata, 132
Mica, 317
Micaceous iron-ore, 349
Microcosmic salt, as blow-pipe-reagent, 107
 preparation, 277
Milk of lime, 291
Milk of sulphur, preparation, 255
Mineral, chameleon, 359
 green, 384
 waters, 122
 analysis, 628
 yellow, 478
Minerals of gold, 398
Mine-tin, 426
Minium, 477
Mirrors, manufacture, 466
Mispickel, 487
Mitscherlich's lamp, 102
Moiré métallique, 421
Molybdates, 447
Molybdena, 446
Molybdenum, 446
 bichloride, 448
 binoxide, 447
 bisulphide, 448
 blue oxide, 447
 green oxide, 447
 oxide, 446
 oxychloride, 448
 protochloride, 448
 reactions, 448
Molybdic acid, 447
Molybdic oxide, 447
Monobasic acid, definition, 40
Monometaphosphoric acid, 178
Morass-ore, 349
Mortar, 291
Mortars and pestles, 86
Mortars, hydraulic, 291
 of Tournay, 298
Mosaic gold, 425
Mother-liquor, 96
Mountain blue, 382
Muffle, 104
Muriatic acid, 142
 of commerce, 142
Mysorine, 382
NASCENT STATE, 45
Natterer's condensing apparatus, 76
Needle iron-ore, 342
Neutralization, 40

- Newton's fusible alloy, 308
 analysis, 610
 Nickel, 367
Nickel-antimony, 369, 436
Nickel, arsenio-sulphide, 369
 basic sulphate, 368
 chloride, 369
 double sulphates, 368
Nickel-ore, gray, 369
 Nickel, metallurgy, 369
 nitrate, 367
Nickel-ore, gray, 369
 Nickel, oxide, 367
 determination, 587
 reactions, 517
 peroxide, 368
 sesquioxide, 368
 subsulphide, 369
 sulphate, 368
 sulphide, 369
 Niobic acid, 493
 Niobium, 493
 chloride, 493
 sulphide, 493
 Nitrate of
 alumina, 312
 ammonia, 276
 baryta, 283
 binoxide of platinum, 406
 cadmium, 377
 cobalt, 371
 lime, 293
 lithia, 27
 magnesia, 304
 nickel, 367
 oxide of iron, 340
 palladium, 411
 potassa, 234
 sesquioxide of chromium, 329
 iron, 343
 uranium, 336
 silver, 485
 soda, 257
 strontia, 288
 tin, 422
 zinc, 364
 Nitrates, 129
 of bismuth, 391
 copper, 380
 lead, 471
 Nitrates of mercury, 458
 suboxide of mercury, 456
 Nitre, 234
 cubic, 257
 Nitre-earth, lixiviation, 235
 Nitre, examination of, 238
 for blowpipe reagent, 107
 Nitre-heaps, 128
 Nitre, manufacture of, 235
 Nitre-plantations, 235
 Nitre, refining, 235
 refraction, 238
 uses, 237
 Nitric acid, 127
 action of, upon organic substances, 129
 anhydrous, 127
 determination, 599, 619
 examination, 501
 fuming, 180
 hydrated, 128
 preparation, 128
 reactions, 541
 Nitric oxide, 125
 Nitride of chromium, 333
 Nitrification, theory of, 284
 Nitrite of
 ammonia, 275
 potassa, 247
 silver, 485
 Nitrites of lead, 471
 Nitrogen, 123
 and boron, 217
 and sulphur, 166
 binoxide, 125
 chloride, 144
 chlorophosphide, 183
 chlorophosphite, 183
 chlorosulphide, 167
 iodide, 151
 peroxide, 127
 phosphides, 183
 protoxide, 124
 teroxide, 126
 tersulphide, 166
 Nitromuriatic acid, 143
 Nitrosulphates, 166
 Nitrosulphuric acid, 166
 Nitrous acid, 126
 commercial, 130
 Nitrous oxide, 124
 Nomenclature, 47
 Notation, 49

Ochre, yellow, 318
Ochres, 318
 Octohedral borax, 269
 Oil-bath, 82
 Oil-gas, 206
 Oil-lamp, 102
 Oil of vitriol, 160
 distillation, 82
 impurities in, 161
 Olefiant gas, 207
Oligist, 349
Olivine, 308
Oolitic iron-ore, 349
Opal, 219
 Ores of iron, 349
 silver, 490
Orpiment, red, 442
 yellow, 442
Orthite, 324
 Organic acids, analytical classification, 542
Orthoclase, 316
 Osmic acid, 416
Osm-iridium, 415
 Osmious acid, 416
Osmites, 416
 Osmium, 415
 bichloride, 477
 binoxide, 416
 chloride, 417
 oxide, 416
 reactions, 417
 sesquioxide, 416
 Oxalic acid, determination, 596
 reactions, 537
 Oxide, carbonic, 195
 Oxide of
 ammonium, 275
 antimonyle, 480
 cadmium, 376
 didymium, 325
 lanthanum, 325
 platosammonium, 407
 selenium, 169
 thorium, 323
 uranyle, 336
 Oxides of
 antimony, 429
 arsenic, 437
 barium, 282
 bismuth, 391
 calcium, 289
 carbon, 195
 cerium, 325
 chlorine, 187
 chromium, 327
 cobalt, 370
 copper, 378
 gold, 395
 hydrogen, 119
 iodine, 149
 iridium, 414
 iron, 340
 lead, 469
 manganese, 356
 mercury, 455
 molybdenum, 446
 nickel, 367
 nitrogen, 124
 osmium, 416
 palladium, 411
 phosphorus, 175
 platinum, 405
 potassium, 231
 rhodium, 413
 ruthenium, 417
 selenium, 169
 silver, 484
 sodium, 257
 strontium, 288
 sulphur, 156
 tantalum, 493
 tellurium, 449
 tin, 422
 titanium, 451
 tungsten, 444
 uranium, 335
 vanadium, 374
 zinc, 363
 Oxy-amide of mercury, 451

- Oxybromide of phosphorus, 188
 Oxychloride of phosphorus, 182
 Oxychlorides, 145
 of zinc, 365
 Oxygen, 115
 Oxygen, combustion in, 71
 preparation, 115
 Oxyhydrogen blowpipe, 119
 Oxysulphides, 168
 Ozone, 116
 tests for, 117

PACKING, 388
 Palladium, 411
 bichloride, 412
 binoxide, 411
 double-chlorides, 412
 nitrate, 411
 oxide, 411
 protochloride, 412
 reactions, 412
 Papin's digester, 121
 Paracyanogen, 209
 Paris yellow, 478
 Parting of gold, 399
 Patent fuel, 188
 Pattinson's process, 480
 Peacock coal, 187
Peacock-copper-ore, 385
 Pearlashes, 250
 Pearl-white, 392
 Peat, 186
 Pelopic acid, 494
 Pelopium, 494
 Pentathionates, 164
 Pentathionic acid, 164
 Perchlorate of potassa, 249
 Perchlorates, 141
 Perchloric acid, 141
 Perchromic acid, 383
 Perculators, 90
 Percussion-tube composition, 249
Periclinc, 317
Peridote, 308
 Periodate of potassa, 249
 Periodates, 150
 Periodic acid, 150
 Permanganate of
 baryta, 361
 potassa, 360
 silver, 361
 Permanganic acid, 360
Petalite, 274, 317
 Petrifying springs, 300
 Pewter, 427, 481
 analysis, 609
 Philosopher's wool, 362
 Phosgene gas, 197
 Phospham, 183
 Phosphamide, 183
 Phosphate of
 alumina, 316
 baryta, 284
 lithia, 276
 magnesia and ammonia, 307
 manganese, 357
 sesquioxide of iron, 344
 soda and ammonia, 277
 Phosphates, Fleitmann and Henneberg's, 179, 268
 of ammonia, 277
 lime, 298
 magnesia, 306
 soda, 260
 tribasic, 178
 triple, 307
 Phosphatic acid, 176
 Phosphide of
 calcium, 303
 iron, 343
 Phosphides, 184
 of copper, 385
 hydrogen, 179
 nitrogen, 183
 tungsten, 446
 Phosphites, 176
 Phosphoric acid, 176
 anhydrous, 177
 determination, 593
 hydrates, 177
 reactions, 582
 Phosphorous acid, 176
 Phosphorus, 172
 allotropic modifications, 173
 amorphous, 174
 and selenium, 184
 sulphur, 183
 chlorosulphide, 182
 impurities in, 174
 iodides, 183
 oxybromide, 183
 oxychloride, 182
 pentabromide, 183
 pentachloride, 182
 red, 174
 Phosphorus-salt, for blow-pipe reagent, 109
 Phosphorus, suboxide, 175
 terbromide, 183
 Phosphorus, tetrachloride, 181
 white, 173
 Phosphuretted hydrogen,
 gaseous, 180
 liquid, 180
 solid, 180
 Pig-iron, 351
Pimelite, 370
 Pinchbeck, 387
Pipoclay, 318
 Pipette for endometrical experiments, 74
 Pipette, 98
 Pitch, 205
Pitchblende, 385
 Pit-coal, 187
 Plaster casts, 398
 Plaster of Paris, 397
 Platinates, 406
 Plating, 492
 Platinum, 408
 alloys, 410
 Platinum-amalgam, 466
 Platinum, ammoniated protochloride, 407
 ammonia-chloride, 409
 Platinum-bases, 407
 Platinum, bichloride, 408
 double-salts, 409
 binoxide, 406
 determination, 681
 nitrate, 406
 reactions, 522
 sulphate, 406
 bisulphide, 410
 Platinum-black, 404
 action on gases, 404
 Platinum-foil, 106
 Platinum, fulminating, 406
 metallurgy, 410
 Platinum-ores, analysis, 418
 Platinum, oxide, 405
 perchloride, 408
 potassio-chloride, 409
 protochloride, 407
 residues, treatment, 406
 sodio-chloride, 409
 spongy, 408
 sulphide, 409
 uses of, 410
 vessels, precautions in use, 404
 wire, 106
 Platosammonium, oxide, 407
 Plumbago, 185
 Plumbates, 476
 of potassa, 476
 Plumbites, 470
 Pneumatic trough, 68
 Polymerism, 49
 Porcelain, Berlin, 320
 English, 319
 Porcelain-painting, 319
 Porcelain, Réaumur's, 223
Porcelaine-tendre, 321
 Portland cement, 292
 Potash, 231
Potash-abbis, 317
Potash-feldspar, 316
 Potashes, 250
 Potash valuation, 616
 Potassa, 231
 aluminate, 312
 antimoniate, 431
 arseniate, 440
 arsenite, 439
 aurate, 496
 aurosulphite, 496
 bicarbonate, 251
 bichromate, 332

- Potassa, bimetantimoniate,** 482
 bisulphate, 250
 bromate, 249
 carbonate, 250
 caustic, 232
 chlorate, 247
 chlorochromate, 383
 chromate, 381
 determination, 590
 examination, 502
 ferrate, 344
fusa, 233
 hydrate, 232
 hydriodate, 252
 hyperoxymuriate, 247
 hypochlorite, 249
 hyposulphite, 254
 iodate, 249
- Potassa-iron-alum,** 344
- Potassa, manganate,** 359
 metantimoniate, 481
 metastannate, 424
 nitrate, 234
 nitrite, 247
 perchlorate, 249
 periodate, 249
 permanganate, 360
 plumbates, 476
 reactions, 510
 silicates, 251
 stannate, 423
 sulphate, 249
 sulphate and bichromate, 383
 terchromate, 383
 uranate, 337
 uses, 234
- Potassium,** 280
- Potassium-amalgam,** 465
- Potassium, amidide,** 132
 aurochloride, 397
 bisulphide, 255
 borofluoride, 215
 bromide, 252
 chloride, 251
 chloride, combinations, 252
 cyanide, for blowpipe-reagent, 107
 fluoride, 253
 hydrofluante of fluoride, 253
 hydrosulphate of sulphide, 254
 iodide, 252
 impurities in, 252
 valuation, 253
 pentasulphide, 255
 peroxide, 251
 polysulphides, 255
 silicofluoride, 255
 suboxide, 231
 sulphide, 254
- Potassium, sulphocarbonate**
 of sulphide, 254
 tersulphide, 255
Potter's clay, 318
 Pottery, 318
 Pouring, directions for, 86
 Powder of Algaroth, 438
 Precipitates, edulcoration of, 574
 ignition of, 575
 Precipitation defined, 51
 in quantitative analysis, 574
Precipitatum per se, 457
 Preliminary examination for acids, 559
 for bases, 547
Psilomelane, 358
 Puddling process, 352
 Pulverization, 85
Pulvis fulminans, 237
Pumice stone, 317
 Purple of Cassius, 395
 Putty-powder, 423
Puzzolano, 292
Pyrites, arsenical, 437
capillary, 369
cobalt, 373
copper, 385
cubical, 350
iron, 347
magnetic, 348
martial, 347
radiated, 350
tin, 426
Pyrochlorite, 323
Pyrolusite, 358
 Pyrophorus, Magnus's, 389
 Pyrophosphate of soda, 262
 Pyrophosphates, 178
 Pyrophosphoric acid, 178
Pyrozone, 317
- QUALITATIVE analysis, systematic,** 546
 apparatus for, 570
 evaporation in, 572
 ignition in, 573
 operations in, 571
 precipitation in, 574
 solution for, 572
- Quartation of gold,** 401
- Quartz,** 219
 analysis, 594
- Quicklime,** 289
- RAEWSKY'S platinum-base,** 408
- Rain-water,** 121
- Ransome's vitrified cement,** 293
- Reactions of**
 acetic acid, 546
 alumina, 513
 ammonia, 511
- Reactions of**
 antimonie acid, 525
 arsenic acid, 529
 arsenious acid, 525
 baryta, 511
 benzoic acid, 545
 binoxide of platinum, 522
 binoxide of tin, 523
 boracic acid, 534
 carbonic acid, 536
 cerium, 325
 chloric acid, 542
 chromic acid, 535
 citric acid, 544
 didymium, 326
 erbium, 325
 gallic acid, 544
 glucina, 322
 hydriodic acid, 539
 hydrobromic acid, 538
 hydrochloric acid, 537
 hydrocyanic acid, 540
 hydroferricyanic acid, 541
 hydroferrocyanic acid, 541
 hydrofluoric acid, 536
 hydrosulphocyanic acid, 541
 hydrosulphuric acid, 536
 hypochlorous acid, 542
 iridium, 415
 lanthanum, 325
 lime, 512
 lithia, 275
 magnesia, 513
 molybdenum, 448
 nitric acid, 541
 osmium, 417
 oxalic acid, 537
 oxide of cadmium, 521
 cobalt, 516
 copper, 520
 iron, 515
 lead, 530
 manganese, 518
 mercury, 519
 nickel, 517
 silver, 530
 tin, 523
 zinc, 518
 palladium, 412
 phosphoric acid, 532
 potassa, 510
 rhodium, 413
 ruthenium, 418
 sesquioxide of chromium, 514
 iron, 514
 silicic acid, 534
 soda, 511
 strontia, 512
 suboxide of mercury, 530

- Reactions of**
 succinic acid, 545
 sulphuric acid, 582
 sulphurous acid, 535
 tannic acid, 543
 tartaric acid, 548
 tellurium, 450
 terbium, 324
 teroxide of antimony, 524
 bismuth, 520
 gold, 521
 thorina, 324
 titanium, 453
 tungsten, 446
 uranium, 337
 uric acid, 544
 vanadium, 375
 yttria, 324
 zirconia, 323
Reagents,
 definition, 499
 for qualitative analysis, 499
 general definition, 499
 examination, 500
 list, 499
 preparation, 500
 special, definition, 499
 examination, 505
 list, 500
 preparation, 505
Realgar, 442
Réaumur's alloy, 436
Réaumur's porcelain, 223
Receivers, 78
 quilled, 78
 tubulated, 78
Recrystallization, 96
Red antimony-ore, 436
Red copper-ore, 385
Red fire, 288
Red-lead, 477
Red lead-ore, 475
Red-lead, uses of, 477
Red orpiment, 442
Red silver-ore, 439
Reduction, by fusion, 101
 on charcoal, 109
Reduction-tubes, 106
Regulus of antimony, 428
Reinsch's test for arsenic, 527
Reiset's platinum compounds, 407
Resin-gas, 207
Retorts, 79
 filling, 79
 heating, 81
 iron, 59
 protection, 81
 tubulated, 79
Rhodium, 412
 chlorides, 413
 oxide, 413
Rhodium, reactions, 413
 sesquioxide, 413
Rhodiumic acid, 197
Ring-burner, 108
River-water, 122
Roasting in blowpipe-flame, 109
Rock alum, 313
Rochelle salt, analysis, 602
Rock-crystal, 219
Rock-salt, 271
 impurities in, 272
Roll sulphur, 154
Roman alum, 313
Roman cement, 292
Rose's lamp, 102
Ruby, 310, 326
Rupert's drop, 223
Rust, ammonia in, 339
Rusting of iron, 339
Ruthenates, 418
Ruthenic acid, 418
Ruthenium, 417
 binoxide, 417
 bichloride, 418
 chloride, 418
 oxide, 417
 reactions, 418
 sesquichloride, 418
 sesquioxide, 417
Rutile, 450
SAFETY-LAMP, Davy's, 202
Safety-tubes, 60
Sal-alembroth, 468
Sal-ammoniac, 278
Salicor, 263
Sal-prunella, 237
Salt, 271
 definition, 40
 extraction, 272
Salt-glazing, 273
 graduation, 271
 of tartar, 250
Saltpetre, 234
Saltpetre-flour, 236
Saltpetre-rot, 234
Salt-radical, definition, 40
Salt, schlotage, 272
 soccage, 272
Sal volatile, 277
Sand, 219
Sand for glass-making, 224
Sand-trays, 69
Sapphires, 310
Saturation, 90
 defined, 51
 of liquids with solids, 90
Saturn's tree, 469
Scheele's-green, 440
Schweinfurt-green, 440
Sea-salt, 271
Sea-water, 122
Seignette salt, analysis, 602
Seleniate of baryta, 284
Selenic acid, 170
Selenide of lead, 479
Selenides, 171
 of phosphorus, 184
Seleniferous deposit, 169
Selenious acid, 170
Selenite, 296
Selenites, 170
Selenium, 169
 bromides, 171
 chlorides, 171
 flowers, 169
 oxide, 169
 sulphides, 171
Seleniuretted hydrogen, 171
Separating funnel, 93
Separation of
 alumina and potassa, 604
 antimony, lead, and bismuth, 610
 arsenic, cobalt, nickel, and iron, 612
 cadmium and zinc, 608
 chlorine, bromine, and iodine, 627
 chromium and iron, 604
 copper and iron, 608
 copper and silver, 611
 copper, tin, antimony, and lead, 611
 copper, zinc, and nickel, 611
 gold, silver, and copper, 612
 iron, alumina, silica, lime, and magnesia, 605
 lime, magnesia, and sesquioxide of iron, 602
 liquids, 93
 manganese and iron, 608
 mercury and tin, 612
 mercury and zinc, 612
 phosphoric acid and alumina, 606
 potassium and sodium, 602
 silicic acid and alumina, 602
 tin and antimony, 610
 tin, antimony, copper, and bismuth, 609
 tin, copper, lead, and zinc, 611
 tin, lead, and bismuth, 610
Serpentine, 308
Shear-steal, 354
Shells, 299
Shot, manufacture, 432
Sienna, 299
Silica, 219
 hydrates, 219
 soluble, natural deposits, 219

- Silicate of lime, as manure, 219
zirconia, 326
- Silicates, 221
Brauner's method of analyzing, 628
decomposition of by chloride of barium, 286
insoluble, analysis, 621
of alumina, 316
copper, 388
lead, 475
manganese, 357
potassa, 251
sesquioxide of iron, 344
soda, 270
zinc, 365
- Silicic acid, 219
determination, 594
reactions, 534
- Silicofluoride of barium, 287
potassium, 255
- Silicon, 218
and bromine, 227
hydrogen, 226
sulphur, 228
chlorosulphide, 228
terchloride, 226
terfluoride, 227
tersulphide, 228
- Sillimanite*, 316
- Silver, 482
- Silver-amalgams, 466
- Silver-ammonio-chloride, 488
ammonio-nitrate, 486
and copper, alloys, 492
arseniate, 440
binoxide, 487
bromide, 489
carbonate, 487
chloride, 487
chlorobromide, 489
double hyposulphites, 487
extraction, by amalgamation, 490
fluoride, 489
fulminating, 485
- Silver-glance*, 489
- Silver, hyposulphite, 486
iodide, 489
- Silver-lustre, 410
- Silver, metallurgy, 490
- Silver, native*, 490
nitrate, 485
nitrite, 485
- Silver-ores, 490
- Silver, oxide, 484
determination, 576
reactions, 530
permanganate, 361
pure, preparation, 482
residues, treatment, 482
standard, analysis, 612
- Silver, suboxide, 484
sulphate, 487
sulphide, 489
technical history, 492
- Silvering on glass, 492
- Slaked lime, 290
- Smalt, 378
- Smelling-salts, 278
- Smithy-scales, 344
- Soapstone*, 306
- Soap-test, 632
- Soda, 257
acid phosphate, 261
acid pyrophosphate, 262
- Soda-alum, 316
arseniate, 440
- Soda, artificial, from common salt, 264
- Soda-ash, manufacture, 264
- Soda, aurate, 396
- Soda, aurate, 396
biborate, 269
bicarbonate, 268
bimetantimoniate, 432
bisulphate, 260
bisulphite, 259
borate, 269
carbonate, 268
examination, 502
for blowpipe reagent, 106
impurities in, 268
uses, 268
caustic, 257
chlorate, 258
chloride, 258
chromate, 333
common, 261
common phosphate, 260
analysis, 601
determination, 591
dipyrophosphate, 262
- Soda-feldspar*, 317
- Soda, ferrate, 345
hydrate, 257
hypochlorite, 258
hyposulphite, 258
- Soda-lakes, 268
- Soda-liver of sulphur, 273
- Soda, manganate, 360
manufacture of, 264
metaphosphate, 262
nitrate, 257
phosphates, 260
- Soda-process, Tilghman's, 267
- Soda, pure carbonate, 266
pyrophosphate, 262
reactions, 511
sesquicarbonate, 268
sesquisulphate, 260
silicates, 270
stannate, 423
subphosphate, 260
sulphate, 259
sulphite, 259
- Soda, triphosphate, 266
valuation, 618
- Soda-waste, 266
- Sodium, 256
- Sodium-amalgam, 465
- Sodium, aurochloride, 396
bromide, 273
chloride, 271
analysis, 600
uses, 272
fluoride, 273
hydrosulphate of sulphide, 273
iodide, 273
oxide, 257
suboxide, 257
sulphides, 273
peroxide, 271
- Soils, analysis, 635
- Solder, 481
- Soldering, 270
- Solubility, determination, 86
- Solution, 86
at ordinary temperatures, apparatus for, 87
by the aid of heat, apparatus for, 87
in quantitative analysis, 572
in test-tubes, 88
of substances for analysis, 548, 560
promoted, 88
theory of, 51
- Solvents, 87
- Soot, 187
- Spatulas, 85
- Specific gravity, 333
bottle, 85
of a liquid, 85
a powder, 84
a solid, 84
a solid soluble in water, 84
gases, 86
vapors, 86
- Specular iron*, 349
- Speculum-metal, 389
- Speiss*, 370, 373
- Speiss cobalt*, analysis, 612
- Spelter*, 366
- Sphene*, 450
- Spinel*, 312
- Spirit-blowpipe, 111
- Spirit-lamps, 102
- Splint coal, 186
- Spodumene*, 274, 317
- Spring-water, 121
- Stalactites*, 300
- Stalagmites*, 300
- Standard gold, 400
analysis, 612
- Standard silver, 492
analysis, 612

- Stannate of oxide of tin, 423
 potassa, 423
 soda, 423
 Stannic acid, 423
 determination, 582
 Steam, 121
Stearite, 308
 Steel, 354
 blistered, 354
 cast, 354
 decarbonisation, 355
 natural, 354
 properties, 354
 shear, 354
 tempering, 354
Stilbite, 317
 Stills, 77
 Still-worm, 77
 Stirrers, 87
 Stoppers, loosening, 68
 Straining, 92
 Strass, 225
 Stream-tin, 426
 Strontia, 288
 carbonate, 288
 determination, 589
 nitrate, 288
 reactions, 512
 sulphate, 288
Strontianite, 288
 Strontium, 287
 binoxide, 288
 chloride, 288
 sulphides, 288
Struvite, 307
 Stuccoes, 298
 Sublimation, apparatus for,
 84
 directions for, 84
 described, 77
 Substitution-products, 152
 Succinic acid, reactions, 545
 Succussion, prevention, 82
Suffoni, 215
 Sugar-lime, 291
 Sulphamide, 276
 Sulphantimoniate of sulphide
 of sodium, 485
 Sulphantimonic acid, 485
 Sulpharsenates, 443
 Sulpharsenic acid, 442
 Sulpharsenious acid, 442
 Sulpharsenites, 442
 Sulphate of alumina, 812
 ammon, 276
 ammonia, 276
 baryta, analysis, 601
 binoxide of platinum,
 406
 bismuth, 892
 copper, 880
 iron, 840
 lead, 472
 lithia, 275
 magnesia, 805
 Sulphate of manganese, 356
 mercury, 459
 nitric oxide, 166
 oxide of chromium and
 potassa, 383
 protoxide of iron, 340
 sesquioxide of chromi-
 um, 329
 iron, 343
 manganese, 358
 uranium, 387
 silver, 487
 strontia, 288
 suboxide of copper, 379
 mercury, 456
 tin, 422
 zinc, 364
 Sulphates, 162
 of antimony, 480
 baryta, 284
 cadmium, 377
 cobalt, 371
 glucina, 322
 lime, 296
 nickel, 368
 potassa, 249
 soda, 259
 Sulphide of
 aluminum, 321
 boron, 218
 cadmium, 377
 carbon, 212
 cerium, 325
 glucinum, 322
 lead, 478
 magnesium, 309
 molybdenum, 448
 niobium, 493
 nitrogen, 166
 silicon, 228
 silver, 489
 tantalum, 493
 titanium, 452
 vanadium, 374
 Sulphides, 168
 Sulphides of
 ammonium, 280
 antimony, 485
 arsenic, 441
 barium, 286
 bismuth, 392
 calcium, 302
 chromium, 385
 cobalt, 373
 copper, 384
 gold, 398
 iron, 347
 manganese, 361
 mercury, 464
 nickel, 369
 phosphorus, 188
 platinum, 409
 potassium, 253
 selenium, 171
 sodium, 278
 Sulphides of
 strontium, 288
 tellurium, 450
 tin, 425
 tungsten, 446
 uranium, 387
 zinc, 365
 Sulphites, 153
 Sulphocarbonate of potassa,
 255
 Sulphocarbonates, 214
 Sulphocarbonic acid, 212
 Sulphophosphates, 182
 Sulphotungstic acid, 446
 Sulphur, 164
 Sulphur-acids, 168
 Sulphur and boron, 217
 and nitrogen, 166
 and silicon, 228
 and bromine, 168
 and chlorine, 168
 determination, 598
 Sulphuretted hydrogen, 165
 Sulphur, flowers, 164
 for gunpowder, 242
 Sulphuric acid, 159
 anhydrous, 159
 bihydrated, 162
 distillation, 161
 determination, 592
 examination, 500
 fuming, 160
 manufacture, 160
 monohydrated, 161
 reactions, 582
 Nordhausen, 160
 terhydrated, 162
 Sulphur, iodide, 168
 milk of, 154
 preparation, 255
 Sulphurous acid, 157
 bleaching action, 157
 determination, 595
 liquid, 157
 reactions, 585
 Sulphur-salts, 168
 Sulphur, subchloride, 167
 Superphosphate of lime, 299
 Supports for dishes, 88
 funnels, 90
Swamp-ore, 349
 Symbols, 49
 table, 114
 Syphon, for mineral waters,
 682
 Syphons, 92
 Syringe-bottle, 92

 TABLE-BLOWPIPE, 111
Talc, 308
 Tannic acid, reactions, 543
 Tantallic acid, 493
Tantalite, 494
 Tantalum, 493
 protoxide, 493

- Tantalum, sesquichloride, 424
 498
 sesquioxide, 498
 sesquisulphide, 498
 Tartar-emetie, analysis, 609
 Tartaric acid, reactions, 648
 Tartar, salt, 260
 Tartrate of potassa and soda,
 analysis, 602
 Telluretted hydrogen, 450
 Telluric acid, 449
 Tellurides, 450
 Tellurium, 449
 bichloride, 450
 chloride, 450
 reactions, 450
 sulphides, 450
 Tellurous acid, 449
 Tempering of steel, 354
 Terbia, 324
 salts, 324
 Terbium, 328
Tests prepared, 300
 Test for hardness of water,
 632
 Testing, definition, 496
 Tetrametaphosphoric acid,
 178
 Tetrathionates of baryta, 165
 Tetrathionic acid, 165
Thénardite, 259
 Thénard's blue, 378
 Thermometric degrees, con-
 version of, 39
 Thilorier's apparatus, 75
 Thorina, 328
 reactions, 328
 Thorium, 328
Thorite, 328
 Tin, 420
 Tin-amalgam, 466
 Tin and arsenic, 448
 Tin, bichloride, 424
 binocide, 428
 determination, 582
 reactions, 523
 bisulphide, 426
Tinical, 269
 determination of value,
 270
 Tin, chloride, 424
 valuation, 424
 Tinfoil, 427
 Tin, metallurgy, 426
 metastannate of oxide,
 424
 Tinned iron, 427
 Tinning of copper, 389, 427
 pins, 389
 Tin, nitrate, 422
 Tin-ores, assay, 427
 Tin, oxide, 422
 determination, 582
 reactions, 523
 oxychloride, 424
 Tin, perchloride, 424
 Tin-plate, 427
 Tin, protoxide, 422
Tin-pyrates, 426
 Tin, refining, by liqutation,
 426
 by tossing, 427
 sesquioxide, 424
 sesquisulphide, 425
 stannate of oxide, 424
Tin-stone, 428
 Tin, sulphate, 422
 sulphide, 425
 uses, 427
 Titanic acid, 451
Titanic iron, 450
Titanite, 450
 Titanium, 450
 bichloride, 452
 bisulphide, 452
 nitrides, 452
 oxide, 451
 reactions of, 453
 sesquichloride, 452
 sesquioxide, 451
 Tobacco, 387
 white, 448
Tops, 310
Touchstones, 401
 Triads of elements, 152
 Tribasic acid, definition, 40
 phosphates, 179
 phosphoric acid, 178
 Trimetaphosphoric acid, 178
Triplene, 317
 Triphosphate of soda, 260
 Triple phosphate, 307
Tripoli, 219
 Trithionates, 164
 Trithionic acid, 163
Trona, 268
 Tube-holder, 88
 Tubes, sealing of, 112
 Tubing, 60
Tunaberg cobalt, 378
 Tungstates, 445
 Tungsten, 444
 bichloride, 445
 binocide, 444
 bisulphide, 446
 phosphides, 446
 reactions, 445
 terchloride, 446
 tersulphide, 446
 Tungstic acid, 445
 Turbith mineral, 459
 Turner's yellow, 478
 Type-metal, 451
 analysis, 610
 ULTRAMARINE, ANALYSIS, 626
 artificial, 278
 green, 274
 natural, 278
Umber, 318, 350
 Uranyl of potassa, 337
Uranite, 335
 Uranium, 335
 black oxide, 336
 green oxide, 336
Uranium-oxide, 336
 oxide, 335
 oxychloride, 337
 peroxide, 336
 protochloride, 337
 protossequioxides, 336
 reactions, 337
 sesquioxide, 336
 hydrates, 336
 nitrate, 336
 salts, 336
 sulphate, 337
 subchloride, 337
 suboxide, 335
 sulphides, 337
Uranium-vitriol, 336
Uranium-oxides, 335
 Uranyl, 336
 chloride, 337
 oxide, 336
Urea, 368
 Uric acid, reactions, 544
 Urinometer, 36
 VALUATION OF AURIFEROUS
 ORES, 402
 Vanadates, 374
 Vanadic oxide, 374
 Vanadium, 374
 binocide, 374
 bisulphide, 374
 protoxide, 374
 reactions, 375
 terchloride, 374
 Vapor-densities, determina-
 tion of, 186
Variagated copper-ore, 385
 Vegetables, incineration, 640
 Vermilion, 464
 impurities in, 465
 Vesicular vapor, 121
 Vitriified borax, 270
 Vitriol, blue, 380
Vitriol-oxide, 343
 WASHING BOTTLE, 92, 497
 Washing by decantation, 92
 Water, 119
 Water-bath, 82
 Water, decomposition, 120
 at high temperatures,
 121
 formation, 119
 Water-gas, 207
 Water, hard and soft, 122
 of constitution, 56
 determination, 601
 of crystallization, 56
 determination, 601
 of hydration, 56

- Water-oven, 95
 Waters, acidulous, 122
 analysis, 628
 carbonated, 122
 chalybeate, 122
 saline, 122
 sulphurous, 122
Wavellite, 316
 analysis, 606
 Weighing, 571
 precipitates, 575
 Welsh coal, 187
 Welter's safety-tube, 60
White antimony-ore, 429
 White lead, 473
 examination, 474
 manufacture, 478
White lead-ore, 478
 White lead, uses, 474
 White precipitate, 462
 White vitriol, 364
Witherite, 285
- Wolfram*, 445
 Wood-charcoal, 191
 Woulfe's bottle, 64
 Wrought iron, 353
- Yellow orpiment*, 442
Yttria, 324
 reactions, 324
 salts, 324
Yttrium, 323
Ytrocrite, 324
Ytrotantalite, 494
- ZAFFRE**, 378
 Zeolites, 221
 Zinc, 362
 Zinc-amalgam, 465
 Zinc, binoxide, 365
Zinc-blende, 365
 Zinc, butter, 365
 carbonate, 364
 double compounds, 364
- Zinc, chloride, 365
Zinc-glance, 365
 Zinc, metallurgy, 366
 nitrate, 364
 Zinc-ores, assay, 366
 Zinc, oxide, 363
 determination, 588
 reactions, 518
 oxychlorides, 365
 oxysulphide, 366
 silicate, 365
 suboxide, 363
 sulphate, 364
 sulphide, 365
 uses, 366
 Zinc-white, 363
Zircon, 326
Zirconia, 326
 reactions, 326
 salts, 326
 silicate, 326
 Zirconium, 326

THE END.



BLANCHARD & LEA'S MEDICAL AND SURGICAL PUBLICATIONS.

TO THE MEDICAL PROFESSION.

In the present catalogue we have affixed prices to our publications, in obedience to the repeated requests of numerous members of the profession. While books, like all other articles, must necessarily vary somewhat in cost throughout the extended territories of this country, yet our publications will generally be furnished at these rates by booksellers throughout the Union, who can readily and speedily procure any which they may not have on hand.

To accommodate those physicians who have not convenient access to bookstores, or who cannot order through merchants visiting the larger cities, we will forward our works by mail, *free of postage*, on receipt of the printed prices in current funds or postage stamps. As our business is wholesale, and we open accounts with booksellers only, the amount must in every case, without exception, accompany the order, and we can assume no risks of the mail, either on the money or the books; and as we sell only our own publications, we can supply no others. Physicians will, therefore, see the convenience and advantage of making their purchases, whenever practicable, from the nearest bookseller.

We can only add that no exertions are spared to merit a continuance of the gratifying confidence hitherto manifested by the profession in all works bearing our imprint.

BLANCHARD & LEA.

PHILADELPHIA, February, 1859.

* * We have just ready a new **ILLUSTRATED CATALOGUE** of our Medical and Scientific Publications, forming an octavo pamphlet of 80 large pages, containing specimens of illustrations, notices of the medical press, &c. &c. It has been prepared without regard to expense, and will be found one of the handsomest specimens of typographical execution as yet presented in this country. Copies will be sent to any address, by mail, free of postage, on receipt of nine cents in stamps.

Catalogues of our numerous publications in miscellaneous and educational literature forwarded on application.

TWO MEDICAL PERIODICALS, FREE OF POSTAGE, FOR FIVE DOLLARS PER ANNUM.

THE AMERICAN JOURNAL OF THE MEDICAL SCIENCES, subject to postage, when not paid for in advance, - - - - - \$5 00
THE MEDICAL NEWS AND LIBRARY, invariably in advance, - - - - - 1 00
 or, BOTH PERIODICALS furnished, **FREE OF POSTAGE**, for Five Dollars remitted in advance.

THE AMERICAN JOURNAL OF THE MEDICAL SCIENCES, EDITED BY ISAAC HAYS, M. D.,

is published Quarterly, on the first of January, April, July, and October. Each number contains at least two hundred and eighty large octavo pages, handsomely and appropriately illustrated, wherever necessary. It has now been issued regularly for more than **THIRTY-FIVE** years, and it has been under the control of the present editor for more than a quarter of a century. Throughout this long period, it has maintained its position in the highest rank of medical periodicals both at home and abroad, and has received the cordial support of the entire profession in this country. Its list of Collaborators will be found to contain a large number of the most distinguished names of the profession in every section of the United States, rendering the department devoted to

ORIGINAL COMMUNICATIONS

full of varied and important matter, of great interest to all practitioners.

As the aim of the Journal, however, is to combine the advantages presented by all the different varieties of periodicals, in its

REVIEW DEPARTMENT

will be found extended and impartial reviews of all important new works, presenting subjects of novelty and interest, together with very numerous

BIBLIOGRAPHICAL NOTICES,

including nearly all the medical publications of the day, both in this country and Great Britain, with a choice selection of the more important continental works. This is followed by the

QUARTERLY SUMMARY,

being a very full and complete abstract, methodically arranged, of the

IMPROVEMENTS AND DISCOVERIES IN THE MEDICAL SCIENCES.

This department of the Journal, so important to the practising physician, is the object of especial care on the part of the editor. It is classified and arranged under different heads, thus facilitating the researches of the reader in pursuit of particular subjects, and will be found to present a very full and accurate digest of all observations, discoveries, and inventions recorded in every branch of medical science. The very extensive arrangements of the publishers are such as to afford to the editor complete materials for this purpose, as he not only regularly receives

ALL THE AMERICAN MEDICAL AND SCIENTIFIC PERIODICALS,

but also twenty or thirty of the more important Journals issued in Great Britain and on the Continent, thus enabling him to present in a convenient compass a thorough and complete abstract of everything interesting or important to the physician occurring in any part of the civilized world.

To their old subscribers, many of whom have been on their list for twenty or thirty years, the publishers feel that no promises for the future are necessary; but those who may desire for the first time to subscribe, can rest assured that no exertion will be spared to maintain the Journal in the high position which it has occupied for so long a period.

By reference to the terms it will be seen that, in addition to this large amount of valuable and practical information on every branch of medical science, the subscriber, by paying in advance, becomes entitled, without further charge, to

THE MEDICAL NEWS AND LIBRARY,

a monthly periodical of thirty-two large octavo pages. Its "NEWS DEPARTMENT" presents the current information of the day, while the "LIBRARY DEPARTMENT" is devoted to presenting standard works on various branches of medicine. Within a few years, subscribers have thus received, without expense, the following works which have passed through its columns:—

WATSON'S LECTURES ON THE PRACTICE OF PHYSIC.

BRODIE'S CLINICAL LECTURES ON SURGERY.

TODD AND BOWMAN'S PHYSIOLOGICAL ANATOMY AND PHYSIOLOGY OF MAN.

WEST'S LECTURES ON THE DISEASES OF INFANCY AND CHILDHOOD.

MALGAIGNE'S OPERATIVE SURGERY, with wood-cuts.

SIMON'S LECTURES ON GENERAL PATHOLOGY.

BENNETT ON PULMONARY TUBERCULOSIS, with wood-cuts,

WEST ON ULCERATION OF THE OS UTERI.

BROWN ON THE SURGICAL DISEASES OF FEMALES, with wood-cuts, and

WEST ON DISEASES OF WOMEN, Part I. (See p. 32.)

While in the number for January, 1858, is commenced a new and highly important work,

HABERSHON ON DISEASES OF THE ALIMENTARY CANAL.

It will be seen that this treatise covers the whole ground of affections of the Digestive Organs, which furnish so very large a portion of the daily practice of the physician. The author's position in Guy's Hospital, and the fact that the work has only just appeared in London, are sufficient guarantee that it is up to the hour, and presents the most advanced condition of this department of medical science, while its thorough practical character is manifested by the great number of cases to which it is founded, no less than one hundred and sixty-three being carefully analyzed in all the details, throughout its pages. It is therefore hoped that it will be found to fully maintain the valuable practical character of the works heretofore presented to subscribers through this medium.

It will thus be seen that for the small sum of FIVE DOLLARS, paid in advance, the subscriber will obtain a Quarterly and a Monthly periodical,

EMBRACING NEARLY SIXTEEN HUNDRED LARGE OCTAVO PAGES,

mailed to any part of the United States, free of postage.

These very favorable terms are now presented by the publishers with the view of removing all difficulties and objections to a full and extended circulation of the Medical Journal to the office of every member of the profession throughout the United States. The rapid extension of mail facilities will now place the numbers before subscribers with a certainty and dispatch not heretofore attainable; while by the system now proposed, every subscriber throughout the Union is placed upon an equal footing, at the very reasonable price of Five Dollars for two periodicals, without further expense.

Those subscribers who do not pay in advance will bear in mind that their subscription of Five Dollars will entitle them to the Journal only, without the News, and that they will be at the expense of their own postage on the receipt of each number. The advantage of a remittance when ordering the Journal will thus be apparent.

As the Medical News and Library is in no case sent without advance payment, its subscribers will always receive it free of postage.

Remittances of subscriptions can be mailed at our risk, when a certificate is taken from the Postmaster that the money is duly inclosed and forwarded.

Address **BLANCHARD & LEA, PHILADELPHIA.**

ALLEN (J. M.), M. D.,

Professor of Anatomy in the Pennsylvania Medical College, &c.

THE PRACTICAL ANATOMIST; or, The Student's Guide in the Dissecting-Room. With 266 illustrations. In one handsome royal 12mo. volume, of over 600 pages, leather. \$2 25.

In the arrangement of this work, the author has endeavored to present a complete and thorough course of dissections in a clearer and more available form for practical use, than has as yet been accomplished. The chapters follow each other in the order in which dissections are usually conducted in this country, and as each region is taken up, every detail regarding it is fully described and illustrated, so that the student is not interrupted in his labors, by the necessity of referring from one portion of the volume to another.

However valuable may be the "Dissector's Guides" which we, of late, have had occasion to notice, we feel confident that the work of Dr. Allen is superior to any of them. We believe with the author, that none is so fully illustrated as this, and the arrangement of the work is such as to facilitate the labors of the student in acquiring a thorough practical knowledge of Anatomy. We most cordially recommend it to their attention.—*Western Lancet*, Dec. 1856.

We believe it to be one of the most useful works upon the subject ever written. It is handsomely illustrated, well printed, and will be found of convenient size for use in the dissecting-room.—*Med. Examiner*, Dec. 1856.

From Prof. J. S. Davis, University of Va.

I am not acquainted with any work that attains so fully the object which it proposes.

From C. P. Fessner, M. D., Demonstrator, University of Michigan.

I have examined the work briefly, but even this examination has convinced me that it is an excellent guide for the Dissector. Its illustrations are beautiful, and more than I have seen in a work of this kind. I shall take great pleasure in recommending it to my classes as the text-book of the dissecting-room.

ANALYTICAL COMPENDIUM

OF MEDICAL SCIENCE, containing Anatomy, Physiology, Surgery, Midwifery, Chemistry, Materia Medica, Therapeutics, and Practice of Medicine. By JOHN NEILL, M. D., and F. G. SMITH, M. D. New and enlarged edition, one thick volume royal 12mo. of over 1000 pages, with 374 illustrations. \$3 00. See NEILL, p. 24.

ABEL (F. A.), F. C. S. AND C. L. BLOXAM.

HANDBOOK OF CHEMISTRY, Theoretical, Practical, and Technical; with a Recommendatory Preface by Dr. HOFMANN. In one large octavo volume, extra cloth, of 682 pages, with illustrations. \$3 25.

ASHWELL (SAMUEL), M. D.,

Obstetric Physician and Lecturer to Gay's Hospital, London.

A PRACTICAL TREATISE ON THE DISEASES PECULIAR TO WOMEN.

Illustrated by Cases derived from Hospital and Private Practices. Third American, from the Third and revised London edition. In one octavo volume, extra cloth, of 528 pages. \$3 00.

The most useful practical work on the subject in the English language.—*Boston Med. and Surg. Journal*.

The most able, and certainly the most standard and practical, work on female diseases that we have yet seen.—*Medico-Chirurgical Review*.

ARNOTT (NEILL), M. D.

ELEMENTS OF PHYSICS; or Natural Philosophy, General and Medical.

Written for universal use, in plain or non-technical language. A new edition, by ISAAC HAYS, M. D. Complete in one octavo volume, leather, of 484 pages, with about two hundred illustrations. \$2 50.

BUDD (GEORGE), M. D., F. R. S.,

Professor of Medicine in King's College, London.

ON DISEASES OF THE LIVER. Third American, from the third and enlarged London edition. In one very handsome octavo volume, extra cloth, with four beautifully colored plates, and numerous wood-cuts. pp. 500. \$3 00. (*Just Issued.*)

Has fairly established for itself a place among the classical medical literature of England.—*British and Foreign Medico-Chir. Review*, July, 1857.

Dr. Budd's Treatise on Diseases of the Liver is now a standard work in Medical literature, and during the intervals which have elapsed between the successive editions, the author has incorporated into the text the most striking novelties which have characterized the recent progress of hepatic physiology and pathology; so that although the size of the book

is not perceptibly changed, the history of liver diseases is made more complete, and is kept upon a level with the progress of modern science. It is the best work on Diseases of the Liver in any language.—*London Med. Times and Gazette*, June 27, 1857.

This work, now the standard book of reference on the diseases of which it treats, has been carefully revised, and many new illustrations of the views of the learned author added in the present edition.—*Dublin Quarterly Journal*, Aug. 1857.

BY THE SAME AUTHOR.

ON THE ORGANIC DISEASES AND FUNCTIONAL DISORDERS OF THE STOMACH. In one neat octavo volume, extra cloth. \$1 50.

From the high position occupied by Dr. Budd as a teacher, a writer, and a practitioner, it is almost needless to state that the present book may be consulted with great advantage. It is written in an easy

style, the subjects are well arranged, and the practical precepts, both of diagnosis and treatment, denote the character of a thoughtful and experienced physician.—*London Med. Times and Gazette*.

BUCKNILL (J. C.), M. D.,
 Medical Superintendent of the Devon County Lunatic Asylum; and
DANIEL H. TUKE, M. D.,
 Visiting Medical Officer to the York Retreat.

A MANUAL OF PSYCHOLOGICAL MEDICINE; containing the History, Nosology, Description, Statistics, Diagnosis, Pathology, and Treatment of **INSANITY.** With a Plate. In one handsome octavo volume, of 536 pages. \$3 00. (*Now Ready, July, 1858.*)

The increase of mental disease in its various forms, and the difficult questions to which it is constantly giving rise, render the subject one of daily enhanced interest, requiring on the part of the physician a constantly greater familiarity with this, the most perplexing branch of his profession. At the same time there has been for some years no work accessible in this country, presenting the results of recent investigations in the Diagnosis and Prognosis of Insanity, and the greatly improved methods of treatment which have done so much in alleviating the condition or restoring the health of the insane. To fill this vacancy the publishers present this volume, assured that the distinguished reputation and experience of the authors will entitle it at once to the confidence of both student and practitioner. Its scope may be gathered from the declaration of the authors that "their aim has been to supply a text book which may serve as a guide in the acquisition of such knowledge, sufficiently elementary to be adapted to the wants of the student, and sufficiently modern in its views and explicit in its teaching to suffice for the demands of the practitioner."

BENNETT (J. HUGHES), M. D., F. R. S. E.,
 Professor of Clinical Medicine in the University of Edinburgh, &c.
THE PATHOLOGY AND TREATMENT OF PULMONARY TUBERCULOSIS, and on the Local Medication of Pharyngeal and Laryngeal Diseases frequently mistaken for or associated with, Phthisis. One vol. 8vo., extra cloth, with wood-cuts. pp. 130. \$1 25.

BENNETT (HENRY), M. D.
A PRACTICAL TREATISE ON INFLAMMATION OF THE UTERUS, ITS CERVIX AND APPENDAGES, and on its connection with Uterine Disease. New and much enlarged edition, preparing by the author for publication in 1859.

We are firmly of opinion that in proportion as a knowledge of uterine diseases becomes more appreciated, this work will be proportionally established as a text-book in the profession.—*The Lancet.*

When, a few years back, the first edition of the present work was published, the subject was almost entirely unknown to the obstetrical celebrities

of the day; and even now we have reason to know that the bulk of the profession are not fully alive to the importance and frequency of the disease of which it takes cognizance. The present edition is so much enlarged, altered, and improved, that it can scarcely be considered the same work.—*Dr. Keating's Abstract.*

BY THE SAME AUTHOR.

A REVIEW OF THE PRESENT STATE OF UTERINE PATHOLOGY.
 Svo., 75 pages, flexible cloth, 50 cents.

BIRD (GOLDING), A. M., M. D., &c.
URINARY DEPOSITS: THEIR DIAGNOSIS, PATHOLOGY, AND THERAPEUTICAL INDICATIONS. A new and enlarged American, from a late improved London edition. With over sixty illustrations. In one royal 12mo. vol, extra cloth. pp. 372. \$1 30

It can scarcely be necessary for us to say anything of the merits of this well-known Treatise, which so admirably brings into practical application the results of those microscopical and chemical researches regarding the physiology and pathology of the urinary secretion, which have contributed so much to the increase of our diagnostic powers, and to the

extension and satisfactory employment of our therapeutic resources. In the preparation of this new edition of his work, it is obvious that Dr. Golding Bird has spared no pains to render it a faithful representation of the present state of scientific knowledge on the subject it embraces.—*The British and Foreign Medico-Chirurgical Review.*

BOWMAN (JOHN E.), M. D.
PRACTICAL HANDBOOK OF MEDICAL CHEMISTRY. Second American, from the third and revised English Edition. In one neat volume, royal 12mo., extra cloth, with numerous illustrations. pp. 288. \$1 25.

BY THE SAME AUTHOR.

INTRODUCTION TO PRACTICAL CHEMISTRY, INCLUDING ANALYSIS. Second American, from the second and revised London edition. With numerous illustrations. In one neat vol., royal 12mo., extra cloth. pp. 350. \$1 25.

SEALE ON THE LAWS OF HEALTH IN RELATION TO MIND AND BODY. A Series of Letters from an old Practitioner to a Patient. In one volume, royal 12mo., extra cloth. pp. 296. 80 cents.

BUSHNAN'S PHYSIOLOGY OF ANIMAL AND VEGETABLE LIFE; a Popular Treatise on the Functions and Phenomena of Organic Life. In one handsome royal 12mo. volume, extra cloth, with over 100 illustrations. pp. 234. 80 cents.

BUCKLER ON THE ETIOLOGY, PATHOLOGY, AND TREATMENT OF FIBRO-BRONCHITIS AND RHEUMATIC PNEUMONIA. In one 8vo. volume, extra cloth. pp. 150. \$1 25.

BLOOD AND URINE (MANUALS ON). BY JOHN WILLIAM GRIFFITH, G. OWEN REESE, AND ALFRED MARKWICK. One thick volume, royal 12mo., extra cloth, with plates. pp. 460. \$1 25.

BRODIE'S CLINICAL LECTURES ON SURGERY. 1 vol. 8vo. cloth. 350 pp. \$1 25.

BARCLAY (A. W.) M. D.,
Assistant Physician to St. George's Hospital, &c.

A MANUAL OF MEDICAL DIAGNOSIS; being an Analysis of the Signs and Symptoms of Disease. In one neat octavo volume, extra cloth, of 424 pages. \$2 00. (*A new work, now ready.*)

Of works exclusively devoted to this important branch, our profession has at command, comparatively, but few, and, therefore, in the publication of the present work, Messrs. Blanchard & Lea have conferred a great favor upon us. Dr. Barclay, from having occupied, for a long period, the position of Medical Registrar at St. George's Hospital, possessed advantages for correct observation and reliable conclusions, as to the significance of symptoms, which have fallen to the lot of but few, either in his own or any other country. He has carefully systematized the results of his observation of over twelve thousand patients, and by his diligence and judicious classification, the profession has been presented with the most convenient and reliable work on the subject of Diagnosis that it has been our good fortune ever to examine; we can, therefore, say of Dr. Barclay's work, that, from his systematic manner of arrangement, his work is one of the best works "for reference" in the daily emergencies of the practitioner, with which we are acquainted; but, at the same time, we would recommend our readers, especially the younger ones, to read thoroughly and study diligently the *wholes* work, and the "emergencies" will not occur so often.—*Southern Med. and Surg. Journ.*, March, 1859.

To give this information, to supply this admitted

deficiency, is the object of Dr. Barclay's Manual. The task of composing such a work is neither an easy nor a light one; but Dr. Barclay has performed it in a manner which meets our most unqualified approbation. He is no mere theorist; he knows his work thoroughly, and in attempting to perform it, has not exceeded his powers.—*British Med. Journal*, Dec. 6, 1857.

We venture to predict that the work will be deservedly popular, and soon become, like Watson's Practice, an indispensable necessity to the practitioner.—*N. A. Med. Journal*, April, 1858.

An inestimable work of reference for the young practitioner and student.—*Nashville Med. Journal*, May, 1858.

We hope the volume will have an extensive circulation, not among students of medicine only, but practitioners also. They will never regret a faithful study of its pages.—*Cincinnati Lancet*, Mar. '68.

This Manual of Medical Diagnosis is one of the most scientific, useful, and instructive works of its kind that we have ever read, and Dr. Barclay has done good service to medical science in collecting, arranging, and analyzing the signs and symptoms of so many diseases.—*N. J. Med. and Surg. Reporter*, March, 1858.

BARLOW (GEORGE H.), M. D.
Physician to Guy's Hospital, London, &c.

A MANUAL OF THE PRACTICE OF MEDICINE. With Additions by D. F. CONDIE, M. D., author of "A Practical Treatise on Diseases of Children," &c. In one handsome octavo volume, leather, of over 600 pages. \$2 75.

We recommend Dr. Barlow's Manual in the warmest manner as a most valuable *vide-mecum*. We have had frequent occasion to consult it, and have found it clear, concise, practical, and sound. It is eminently a practical work, containing all that is essential, and avoiding useless theoretical discussion. The work supplies what has been for some time wanting, a manual of practice based upon modern discoveries in pathology and rational views of treatment of disease. It is especially intended for the use of students and junior practitioners, but it

will be found hardly less useful to the experienced physician. The American editor has added to the work three chapters—on Cholera Infantum, Yellow Fever, and Cerebro-spinal Meningitis. These additions, the two first of which are indispensable to a work on practice destined for the profession in this country, are executed with great judgment and fidelity, by Dr. Condie, who has also succeeded happily in imitating the conciseness and clearness of style which are such agreeable characteristics of the original book.—*Boston Med. and Surg. Journal*.

BARTLETT (ELISHA), M. D.

THE HISTORY, DIAGNOSIS, AND TREATMENT OF THE FEVERS OF THE UNITED STATES. A new and revised edition. By ALONZO CLARK, M. D., Prof. of Pathology and Practical Medicine in the N. Y. College of Physicians and Surgeons, &c. In one octavo volume, of six hundred pages, extra cloth. Price \$3 00.

It is the best work on fevers which has emanated from the American press, and the present editor has carefully availed himself of all information existing upon the subject in the Old and New World, so that the doctrines advanced are brought down to the latest date in the progress of this department of Medical Science.—*London Med. Times and Gazette*, May 2, 1857.

This excellent monograph on febrile disease, has stood deservedly high since its first publication. It will be seen that it has now reached its fourth edition under the supervision of Prof. A. Clark, a gentleman who, from the nature of his studies and pursuits, is well calculated to appreciate and discuss the many intricate and difficult questions in patho-

logy. His annotations add much to the interest of the work, and have brought it well up to the condition of the science as it exists at the present day in regard to this class of diseases.—*Southern Med. and Surg. Journal*, Mar. 1857.

It is a work of great practical value and interest, containing much that is new relative to the several diseases of which it treats, and, with the additions of the editor, is fully up to the times. The distinctive features of the different forms of fever are plainly and forcibly portrayed, and the lines of demarcation carefully and accurately drawn, and to the American practitioner is a more valuable and safe guide than any work on fever extant.—*Ohio Med. and Surg. Journal*, May, 1857.

BROWN (ISAAC BAKER),
Surgeon-Accoucheur to St. Mary's Hospital, &c.

ON SOME DISEASES OF WOMEN ADMITTING OF SURGICAL TREATMENT. With handsome illustrations. One vol. 8vo., extra cloth, pp. 276. \$1 60.

Mr. Brown has earned for himself a high reputation in the operative treatment of sundry diseases and injuries to which females are peculiarly subject. We can truly say of his work that it is an important addition to obstetrical literature. The operative suggestions and contrivances which Mr. Brown describes, exhibit much practical sagacity and skill,

and merit the careful attention of every surgeon-accoucheur.—*Association Journal*.

We have no hesitation in recommending this book to the careful attention of all surgeons who make female complaints a part of their study and practice.—*Dublin Quarterly Journal*.

CARPENTER (WILLIAM B.), M. D., F. R. S., &c.,
 Examiner in Physiology and Comparative Anatomy in the University of London.

PRINCIPLES OF HUMAN PHYSIOLOGY; with their chief applications to Psychology, Pathology, Therapeutics, Hygiene, and Forensic Medicine. A new American, from the last and revised London edition. With nearly three hundred illustrations. Edited, with additions, by FRANCIS GURNEY SMITH, M. D., Professor of the Institutes of Medicine in the Pennsylvania Medical College, &c. In one very large and beautiful octavo volume, of about nine hundred large pages, handsomely printed and strongly bound in leather, with raised bands. \$4 25.

In the preparation of this new edition, the author has spared no labor to render it, as heretofore, a complete and lucid exposition of the most advanced condition of its important subject. The amount of the additions required to effect this object thoroughly, joined to the former large size of the volume, presenting objections arising from the unwieldy bulk of the work, he has omitted: those portions not bearing directly upon HUMAN PHYSIOLOGY, designing to incorporate them in his forthcoming Treatise on GENERAL PHYSIOLOGY. As a full and accurate text-book on the Physiology of Man, the work in its present condition therefore presents even greater claims upon the student and physician than those which have heretofore won for it the very wide and distinguished favor which it has so long enjoyed. The additions of Prof. Smith will be found to supply whatever may have been wanting to the American student, while the introduction of many new illustrations, and the most careful mechanical execution, render the volume one of the most attractive as yet issued.

For upwards of thirteen years Dr. Carpenter's work has been considered by the profession generally, both in this country and England, as the most valuable compendium on the subject of physiology in our language. This distinction it owes to the high attainments and unwearied industry of its accomplished author. The present edition (which, like the last American one, was prepared by the author himself), is the result of such extensive revision, that it may almost be considered a new work. We need hardly say, in concluding this brief notice, that while the work is indispensable to every student of medicine in this country, it will amply repay the practitioner for its perusal by the interest and value of its contents.—*Boston Med. and Surg. Journal.*

This is a standard work—the text-book used by all medical students who read the English language. It has passed through several editions in order to keep pace with the rapidly growing science of Physiology. Nothing need be said in its praise, for its merits are universally known; we have nothing to say of its defects, for they only appear where the science of which it treats is incomplete.—*Western Lancet.*

The most complete exposition of physiology which any language can at present give.—*Brit. and For. Med.-Chirurg. Review.*

The greatest, the most reliable, and the best book on the subject which we know of in the English language.—*Stethoscope.*

To enlarge this great work would be superfluous. We should observe, however, that in this edition the author has remodelled a large portion of the former, and the editor has added much matter of interest, especially in the form of illustrations. We may confidently recommend it as the most complete work on Human Physiology in our language.—*Southern Med. and Surg. Journal*, December, 1855.

The most complete work on the science in our language.—*Am. Med. Journal.*

The most complete work now extant in our language.—*N. O. Med. Register.*

The best text-book in the language on this extensive subject.—*London Med. Times.*

A complete encyclopedia of this branch of science.—*N. Y. Med. Times.*

The profession of this country, and perhaps also of Europe, have anxiously and for some time awaited the announcement of this new edition of Carpenter's Human Physiology. His former editions have for many years been almost the only text-book on Physiology in all our medical schools, and its circulation among the profession has been unsurpassed by any work in any department of medical science.

It is quite unnecessary for us to speak of this work as its merits would justify. The mere announcement of its appearance will afford the highest pleasure to every student of Physiology, while its perusal will be of infinite service in advancing physiological science.—*Ohio Med. and Surg. Journ.*

BY THE SAME AUTHOR. (*Lately Issued.*)

PRINCIPLES OF COMPARATIVE PHYSIOLOGY. New American, from the Fourth and Revised London edition. In one large and handsome octavo volume, with over three hundred beautiful illustrations. pp. 752. Extra cloth, \$4 80; leather, raised bands, \$5 25.

The delay which has existed in the appearance of this work has been caused by the very thorough revision and remodelling which it has undergone at the hands of the author, and the large number of new illustrations which have been prepared for it. It will, therefore, be found almost a new work, and fully up to the day in every department of the subject, rendering it a reliable text-book for all students engaged in this branch of science. Every effort has been made to render its typographical finish and mechanical execution worthy of its exalted reputation, and creditable to the mechanical arts of this country.

This book should not only be read but thoroughly studied by every member of the profession. None are too wise or old, to be benefited thereby. But especially to the younger class would we cordially commend it as best fitted of any work in the English language to qualify them for the reception and comprehension of those truths which are daily being developed in physiology.—*Medical Counsellor.*

Without pretending to it, it is an encyclopedia of the subject, accurate and complete in all respects—a truthful reflection of the advanced state at which the science has now arrived.—*Dublin Quarterly Journal of Medical Science.*

A truly magnificent work—in itself a perfect physiological study.—*Ranking's Abstract.*

This work stands without its fellow. It is one of the few men in Europe could have undertaken; it is one

no man, we believe, could have brought to so successful an issue as Dr. Carpenter. It required for its production a physiologist at once deeply read in the labors of others, capable of taking a general, critical, and unprejudiced view of those labors, and of combining the varied, heterogeneous materials at his disposal, so as to form an harmonious whole. We feel that this abstract can give the reader a very imperfect idea of the fullness of this work, and no idea of its unity, of the admirable manner in which material has been brought, from the most various sources, to conduce to its completeness, of the lucidity of the reasoning it contains, or of the clearness of language in which the whole is clothed. Not the profession only, but the scientific world at large, must feel deeply indebted to Dr. Carpenter for this great work. It must, indeed, add largely even to his high reputation.—*Medical Times.*

CARPENTER (WILLIAM B.), M. D., F. R. S.,

Examiner in Physiology and Comparative Anatomy in the University of London.

THE MICROSCOPE AND ITS REVELATIONS. With an Appendix containing the Applications of the Microscope to Clinical Medicine, &c. By F. G. SMITH, M. D. Illustrated by four hundred and thirty-four beautiful engravings on wood. In one large and very handsome octavo volume, of 724 pages, extra cloth, \$4 00; leather, \$4 50.

Dr. Carpenter's position as a microscopist and physiologist, and his great experience as a teacher eminently qualify him to produce what has long been wanted—a good text-book on the practical use of the microscope. In the present volume his object has been, as stated in his Preface, "to combine, within a moderate compass, that information with regard to the use of his 'tools,' which is most essential to the working microscopist, with such an account of the objects best fitted for his study, as might qualify him to comprehend what he observes, and might thus prepare him to benefit science, whilst expanding and refreshing his own mind." That he has succeeded in accomplishing this, no one acquainted with his previous labors can doubt.

The great importance of the microscope as a means of diagnosis, and the number of microscopists who are also physicians, have induced the American publishers, with the author's approval, to add an Appendix, carefully prepared by Professor Smith, on the applications of the instrument to clinical medicine, together with an account of American Microscopes, their modifications and accessories. This portion of the work is illustrated with nearly one hundred wood-cuts, and, it is hoped, will adapt the volume more particularly to the use of the American student.

Every care has been taken in the mechanical execution of the work, which is confidently presented as in no respect inferior to the choicest productions of the London press.

The mode in which the author has executed his intentions may be gathered from the following condensed synopsis of the

CONTENTS.

INTRODUCTION—History of the Microscope. CHAP. I. Optical Principles of the Microscope. CHAP. II. Construction of the Microscope. CHAP. III. Accessory Apparatus. CHAP. IV. Management of the Microscope. CHAP. V. Preparation, Mounting, and Collection of Objects. CHAP. VI. Microscopic Forms of Vegetable Life—Protophytes. CHAP. VII. Higher Cryptogamia. CHAP. VIII. Phanerogamic Plants. CHAP. IX. Microscopic Forms of Animal Life—Protozoa—Animalcules. CHAP. X. Foraminifera, Polycystina, and Sponges. CHAP. XI. Zoophytes. CHAP. XII. Echinodermata. CHAP. XIII. Polyzoa and Compound Tunicata. CHAP. XIV. Molluscous Animals Generally. CHAP. XV. Annulosa. CHAP. XVI. Crustacea. CHAP. XVII. Insects and Arachnida. CHAP. XVIII. Vertebrated Animals. CHAP. XIX. Applications of the Microscope to Geology. CHAP. XX. Inorganic or Mineral Kingdom—Polarization. APPENDIX. Microscope as a means of Diagnosis—Injections—Microscopes of American Manufacture.

Those who are acquainted with Dr. Carpenter's previous writings on Animal and Vegetable Physiology, will fully understand how vast a store of knowledge he is able to bring to bear upon so comprehensive a subject as the revelations of the microscope; and even those who have no previous acquaintance with the construction or uses of this instrument, will find abundance of information conveyed in clear and simple language.—*Med. Times and Gazette.*

Although originally not intended as a strictly

medical work, the additions by Prof. Smith give it a positive claim upon the profession, for which we doubt not he will receive their sincere thanks. Indeed, we know not where the student of medicine will find such a complete and satisfactory collection of microscopic facts bearing upon physiology and practical medicine as is contained in Prof. Smith's appendix; and this of itself, it seems to us, is fully worth the cost of the volume.—*Louisville Medical Review*, Nov. 1866.

BY THE SAME AUTHOR.

ELEMENTS (OR MANUAL) OF PHYSIOLOGY, INCLUDING PHYSIOLOGICAL ANATOMY. Second American, from a new and revised London edition. With one hundred and ninety illustrations. In one very handsome octavo volume, leather. pp. 566. \$3 00.

In publishing the first edition of this work, its title was altered from that of the London volume, by the substitution of the word "Elements" for that of "Manual," and with the author's sanction the title of "Elements" is still retained as being more expressive of the scope of the treatise.

To say that it is the best manual of Physiology now before the public, would not do sufficient justice to the author.—*Buffalo Medical Journal.*

In his former works it would seem that he had exhausted the subject of Physiology. In the present, he gives the essence, as it were, of the whole.—*N. Y. Journal of Medicine.*

Those who have occasion for an elementary treatise on Physiology, cannot do better than to possess themselves of the manual of Dr. Carpenter.—*Medical Examiner.*

The best and most complete exposé of modern Physiology, in one volume, extant in the English language.—*St. Louis Medical Journal.*

BY THE SAME AUTHOR. (Preparing.)

PRINCIPLES OF GENERAL PHYSIOLOGY, INCLUDING ORGANIC CHEMISTRY AND HISTOLOGY. With a General Sketch of the Vegetable and Animal Kingdom. In one large and very handsome octavo volume, with several hundred illustrations.

The subject of general physiology having been omitted in the last editions of the author's "Comparative Physiology" and "Human Physiology," he has undertaken to prepare a volume which shall present it more thoroughly and fully than has yet been attempted, and which may be regarded as an introduction to his other works.

BY THE SAME AUTHOR.

A PRIZE ESSAY ON THE USE OF ALCOHOLIC LIQUORS IN HEALTH AND DISEASE. New edition, with a Preface by D. F. CONDRÉ, M. D., and explanations of scientific words. In one neat 12mo. volume, extra cloth. pp. 178. 50 cents.

CONDIE (D. F.), M. D., &c.

A PRACTICAL TREATISE ON THE DISEASES OF CHILDREN. Fifth edition, revised and augmented. In one large volume, 8vo., leather, of over 750 pages. \$3 25. (Now Ready, December, 1858.)

In presenting a new and revised edition of this favorite work, the publishers have only to state that the author has endeavored to render it in every respect "a complete and faithful exposition of the pathology and therapeutics of the maladies incident to the earlier stages of existence—a full and exact account of the diseases of infancy and childhood." To accomplish this he has subjected the whole work to a careful and thorough revision, rewriting a considerable portion, and adding several new chapters. In this manner it is hoped that any deficiencies which may have previously existed have been supplied, that the recent labors of practitioners and observers have been thoroughly incorporated, and that in every point the work will be found to maintain the high reputation it has enjoyed as a complete and thoroughly practical book of reference in infantile affections.

A few notices of previous editions are subjoined.

Dr. Condie's scholarship, acumen, industry, and practical sense are manifested in this, as in all his numerous contributions to science.—*Dr. Holmes's Report to the American Medical Association.*

Taken as a whole, in our judgment, Dr. Condie's Treatise is the one from the perusal of which the practitioner in this country will rise with the greatest satisfaction.—*Western Journal of Medicine and Surgery.*

One of the best works upon the Diseases of Children in the English language.—*Western Lancet.*

We feel assured from actual experience that no physician's library can be complete without a copy of this work.—*N. Y. Journal of Medicine.*

A veritable pædiatric encyclopædia, and an honor to American medical literature.—*Ohio Medical and Surgical Journal.*

We feel persuaded that the American medical profession will soon regard it not only as a very good, but as the VERY BEST "Practical Treatise on the Diseases of Children."—*American Medical Journal.*

In the department of infantile therapeutics, the work of Dr. Condie is considered one of the best which has been published in the English language.—*The Stethoscope.*

We pronounced the first edition to be the best work on the diseases of children in the English language, and, notwithstanding all that has been published, we still regard it in that light.—*Medical Examiner.*

The value of works by native authors on the diseases which the physician is called upon to combat, will be appreciated by all; and the work of Dr. Condie has gained for itself the character of a safe guide for students, and a useful work for consultation by those engaged in practice.—*N. Y. Med. Times.*

This is the fourth edition of this deservedly popular treatise. During the interval since the last edition, it has been subjected to a thorough revision by the author; and all new observations in the pathology and therapeutics of children have been included in the present volume. As we said before, we do not know of a better book on diseases of children, and to a large part of its recommendations we yield an unhesitating concurrence.—*Buffalo Med. Journal.*

Perhaps the most full and complete work now before the profession of the United States; indeed, we may say in the English language. It is vastly superior to most of its predecessors.—*Transylvania Med. Journal.*

CHRISTISON (ROBERT), M. D., V. P. R. S. E., &c.

A DISPENSATORY; or, Commentary on the Pharmacopœias of Great Britain and the United States; comprising the Natural History, Description, Chemistry, Pharmacy, Actions, Uses, and Doses of the Articles of the Materia Medica. Second edition, revised and improved, with a Supplement containing the most important New Remedies. With copious Additions, and two hundred and thirteen large wood-engravings. By R. EGLESFIELD GRIFFITH, M. D. In one very large and handsome octavo volume, leather, raised bands, of over 1000 pages. \$3 50

COOPER (BRANSBY B.), F. R. S.

LECTURES ON THE PRINCIPLES AND PRACTICE OF SURGERY. In one very large octavo volume, extra cloth, of 750 pages. \$3 00.

COOPER ON DISLOCATIONS AND FRACTURES OF THE JOINTS—Edited by BRANSBY B. COOPER, F. R. S., &c. With additional Observations by Prof. J. C. WARREN. A new American edition. In one handsome octavo volume, extra cloth, of about 500 pages, with numerous illustrations on wood. \$3 25.

COOPER ON THE ANATOMY AND DISEASES OF THE BREAST, with twenty-five Miscellaneous and Surgical Papers. One large volume, imperial 8vo., extra cloth, with 254 figures, on 36 plates. \$2 50.

COOPER ON THE STRUCTURE AND DISEASES OF THE TESTIS, AND ON THE THYMUS GLAND. One vol. imperial 8vo., extra cloth, with 177 figures on 29 plates. \$2 00.

COPLAND ON THE CAUSES, NATURE, AND TREATMENT OF PALSY AND APOPLEXY. In one volume, royal 12mo., extra cloth. pp. 36. 80 cents.

CLYMER ON FEVERS; THEIR DIAGNOSIS, PATHOLOGY, AND TREATMENT In one octavo volume, leather, of 600 pages. \$1 50.

COLOMBAT DE L'ISERE ON THE DISEASES OF FEMALES, and on the special Hygiene of their Sex. Translated, with many Notes and Additions, by C. D. MERRIS, M. D. Second edition, revised and improved. In one large volume, octavo, leather, with numerous wood-cuts. pp. 78. \$3 50.

CARSON (JOSEPH), M. D.,

Professor of Materia Medica and Pharmacy in the University of Pennsylvania.

SYNOPSIS OF THE COURSE OF LECTURES ON MATERIA MEDICA AND PHARMACY, delivered in the University of Pennsylvania. Second and revised edition. In one very neat octavo volume, extra cloth, of 208 pages. \$1 50.

CURLING (T. B.), F. R. S.,

Surgeon to the London Hospital, President of the Hunterian Society, &c.

A PRACTICAL TREATISE ON DISEASES OF THE TESTIS, SPERMATIC CORD, AND SCROTUM. Second American, from the second and enlarged English edition. In one handsome octavo volume, extra cloth, with numerous illustrations. pp. 420. \$2 00.

CHURCHILL (FLEETWOOD), M. D., M. R. I. A.
ON THE THEORY AND PRACTICE OF MIDWIFERY. Edited, with
 Notes and Additions, by D. FRANCIS CONDIE, M. D., author of a "Practical Treatise on the
 Diseases of Children," &c. With 139 illustrations. In one very handsome octavo volume,
 leather. pp. 510. \$3 00.

To bestow praise on a book that has received such marked approbation would be superfluous. We need only say, therefore, that if the first edition was thought worthy of a favorable reception by the medical public, we can confidently affirm that this will be found much more so. The lecturer, the practitioner, and the student, may all have recourse to its pages, and derive from their perusal much interest and instruction in everything relating to theoretical and practical midwifery.—*Dublin Quarterly Journal of Medical Science.*

A work of very great merit, and such as we can confidently recommend to the study of every obstetric practitioner.—*London Medical Gazette.*

This is certainly the most perfect system extant. It is the best adapted for the purposes of a text-book, and that which he whose necessities confine him to one book, should select in preference to all others.—*Southern Medical and Surgical Journal.*

The most popular work on midwifery ever issued from the American press.—*Charleston Med. Journal.*

We were reduced to the necessity of having but one work on midwifery, and permitted to choose, we would unhesitatingly take Churchill.—*Western Med. and Surg. Journal.*

It is impossible to conceive a more useful and elegant manual than Dr. Churchill's Practice of Midwifery.—*Provincial Medical Journal.*

Certainly, in our opinion, the very best work on the subject which exists.—*N. Y. Analyst.*

No work holds a higher position, or is more deserving of being placed in the hands of the tyro, the advanced student, or the practitioner.—*Medical Examiner.*

Previous editions, under the editorial supervision of Prof. R. M. Huston, have been received with marked favor, and they deserved it; but this, reprinted from a very late Dublin edition, carefully revised and brought up by the author to the present time, does present an unusually accurate and able exposition of every important particular embraced in the department of midwifery. * * The clearness, directness, and precision of its teachings, together with the great amount of statistical research which its text exhibits, have served to place it already in the foremost rank of works in this department of remedial science.—*N. O. Med. and Surg. Journal.*

In our opinion, it forms one of the best if not the very best text-book and epitome of obstetric science which we at present possess in the English language.—*Monthly Journal of Medical Science.*

The clearness and precision of style in which it is written, and the great amount of statistical research which it contains, have served to place it in the first rank of works in this department of medical science.—*N. Y. Journal of Medicine.*

Few treatises will be found better adapted as a text-book for the student, or as a manual for the frequent consultation of the young practitioner.—*American Medical Journal.*

BY THE SAME AUTHOR. (*Just Issued.*)

ON THE DISEASES OF INFANTS AND CHILDREN. Second American Edition, revised and enlarged by the author. Edited, with Notes, by W. V. KEATING, M. D. In one large and handsome volume, extra cloth, of over 700 pages. \$3 00, or in leather, \$3 25.

In preparing this work a second time for the American profession, the author has spared no labor in giving it a very thorough revision, introducing several new chapters, and rewriting others, while every portion of the volume has been subjected to a severe scrutiny. The efforts of the American editor have been directed to supplying such information relative to matters peculiar to this country as might have escaped the attention of the author, and the whole may, therefore, be safely pronounced one of the most complete works on the subject accessible to the American Profession. By an alteration in the size of the page, these very extensive additions have been accommodated without unduly increasing the size of the work.

This work contains a vast amount of interesting matter, which is so well arranged and so curiously worded that the book may be regarded as an encyclopedia of information upon the subject of which it treats. It is certainly also a monument of Dr. Churchill's untiring industry, inasmuch as there is not a single work upon the diseases of children with which we are acquainted that is not fully referred to and quoted from in its pages, and scarcely a contribution of the least importance to any British or Foreign Medical Journal, for some years past, which is not daily noticed.—*London Lancet*, Feb. 30, 1858.

Availing himself of every fresh source of information, Dr. Churchill endeavored, with his accustomed industry and perseverance, to bring his work up to the present state of medical knowledge in all the subjects of which it treats; and in this endeavor he has, we feel bound to say, been eminently successful. Besides the addition of more than one hundred and thirty pages of matter, we observe that some entirely new and important chapters are introduced, viz: on paralysis, syphilis, phthisis, sclerema, &c. &c. As the work now stands, it is, we believe, the most comprehensive in the English language upon the diseases incident to early life.—*Dublin Quarterly Journal*, Feb. 1858.

It brings before the reader an amount of information not comprised in any similar production in the language. The amount of labor consumed upon its production can only be conceived by those who have been similarly occupied, every work of note published within the last twenty-five years in the different languages of Europe having been laid under

contribution for the illustration of its topics. The material thus derived has been used with consummate skill, and the result has been a work creditable alike to the author and his country.—*N. A. Medico-Chir. Review*, May, 1858.

After this meagre, and we know, very imperfect notice of Dr. Churchill's work, we shall conclude by saying, that it is one that cannot fail from its copiousness, extensive research, and general accuracy, to exalt still higher the reputation of the author in this country. The American reader will be particularly pleased to find that Dr. Churchill has done full justice throughout his work to the various American authors on this subject. The names of Dewees, Eberle, Condie, and Stewart, occur on nearly every page, and these authors are constantly referred to by the author in terms of the highest praise, and with the most liberal courtesy.—*The Medical Examiner.*

We recommend the work of Dr. Churchill most cordially, both to students and practitioners, as a valuable and reliable guide in the treatment of the diseases of children.—*Am. Journ. of the Med. Sciences.*

We know of no work on this department of Practical Medicine which presents so candid and unprejudiced a statement or posting up of our actual knowledge as this.—*N. Y. Journal of Medicine.*

Its claims to merit both as a scientific and practical work, are of the highest order. What we would not elevate it above every other treatise on the same subject, we certainly believe that very few are equal to it, and none superior.—*Southern Med. and Surgical Journal.*

BY THE SAME AUTHOR.

ESSAYS ON THE PUERPERAL FEVER, AND OTHER DISEASES PECULIAR TO WOMEN. Selected from the writings of British Authors previous to the close of the Eighteenth Century. In one neat octavo volume, extra cloth, of about 450 pages. \$2 50.

CHURCHILL (FLEETWOOD), M. D., M. R. I. A., &c.

ON THE DISEASES OF WOMEN; including those of Pregnancy and Child-bed. A new American edition, revised by the Author. With Notes and Additions, by D. FRANKS CONDIE, M. D., author of "A Practical Treatise on the Diseases of Children." With numerous illustrations. In one large and handsome octavo volume, leather, of 768 pages. (Just Issued, 1857.) \$3 00.

This edition of Dr. Churchill's very popular treatise may almost be termed a new work, so thoroughly has he revised it in every portion. It will be found greatly enlarged, and thoroughly brought up to the most recent condition of the subject, while the very handsome series of illustrations introduced, representing such pathological conditions as can be accurately portrayed, present a novel feature, and afford valuable assistance to the young practitioner. Such additions as appeared desirable for the American student have been made by the editor, Dr. Condie, while a marked improvement in the mechanical execution which the volume has undergone, while the price

has been kept at the former very moderate rate. It comprises, unquestionably, one of the most exact and comprehensive expositions of the present state of medical knowledge in respect to the diseases of women that has yet been published.—*Am. Journ. Med. Sciences*, July, 1857.

We hail with much pleasure the volume before us, thoroughly revised, corrected, and brought up to the latest date, by Dr. Churchill himself, and rendered still more valuable by notes, from the experienced and able pen of Dr. D. F. Condie, of Philadelphia.—*Southern Med. and Surg. Journal*, Oct. 1857.

This work is the most reliable which we possess on this subject; and is deservedly popular with the profession.—*Charleston Med. Journal*, July, 1857.

Dr. Churchill's treatise on the *Diseases of Women* is, perhaps, the most popular of his works with the profession in this country. It has been very generally received both as a text-book and manual of practice. The present edition has undergone the most elaborate revision, and additions of an important character have been made, to render it a complete exponent of the present state of our knowledge of these diseases.—*N. Y. Journ. of Med.*, Sept. 1857.

We now regretfully take leave of Dr. Churchill's book. Had our typographical limits permitted, we should gladly have borrowed more from its richly stored pages. In conclusion, we heartily recommend it to the profession, and would at the same time express our firm conviction that it will not only add to the reputation of its author, but will prove a work of great and extensive utility to obstetric practitioners.—*Dublin Medical Press*.

We know of no author who deserves that approbation, on "the diseases of females," to the same

extent that Dr. Churchill does. His, indeed, is the only thorough treatise we know of on the subject; and it may be commended to practitioners and students as a masterpiece in its particular department. The former editions of this work have been commended strongly in this journal, and they have their way to an extended, and a well-deserved popularity. This fifth edition, before us, is well calculated to maintain Dr. Churchill's high reputation. It was revised and enlarged by the author, for his American publishers, and it seems to us that there is scarcely any species of desirable information on its subjects that may not be found in this work.—*The Western Journal of Medicine and Surgery*.

We are gratified to announce a new and revised edition of Dr. Churchill's valuable work on the diseases of females. We have ever regarded it as one of the very best works on the subjects embraced within its scope, in the English language; and the present edition, enlarged and revised by the author, renders it still more entitled to the confidence of the profession. The valuable notes of Prof. Huxley have been retained, and contribute, in no small degree, to enhance the value of the work. It is a source of congratulation that the publishers have permitted the author to be, in this instance, his own editor, thus securing all the revision which an author alone is capable of making.—*The Western Lancet*.

As a comprehensive manual for students, or a work of reference for practitioners, we only speak with common justice when we say that it surpasses any other that has ever issued on the same subject from the British press.—*The Dublin Quarterly Journal*.

DICKSON (S. H.), M. D.,

Professor of Practice of Medicine in the Jefferson Medical College, Philadelphia.

ELEMENTS OF MEDICINE; a Compendious View of Pathology and Therapeutics, or the History and Treatment of Diseases. In one large and handsome octavo volume, of 750 pages, leather. \$3 75.

As an American text-book on the Practice of Medicine for the student, and as a condensed work of reference for the practitioner, this volume will have strong claims on the attention of the profession. Few physicians have had wider opportunities than the author for observation and experience, and few perhaps have used them better. As the result of a life of study and practice, therefore, the present volume will doubtless be received with the welcome it deserves.

This book is eminently what it professes to be; a distinguished merit in these days. Designed for "Teachers and Students of Medicine," and admirably suited to their wants, we think it will be received, on its own merits, with a hearty welcome.—*Boston Med. and Surg. Journal*.

Indited by one of the most accomplished writers of our country, as well as by one who has long held a high position among teachers and practitioners of medicine, this work is entitled to patronage and careful study. The learned author has endeavored to condense in this volume most of the practical matter contained in his former productions, so as to adapt it to the use of those who have not time to devote to more extensive works.—*Southern Med. and Surg. Journal*.

Prof. Dickson's work supplies, to a great extent, a desideratum long felt in American medicine.—*N. O. Med. and Surg. Journal*.

Estimating this work according to the purpose for which it is designed, we must think highly of its

merits, and we have no hesitation in predicting for it a favorable reception by both students and teachers.

Not professing to be a complete and comprehensive treatise, it will not be found full in detail, nor filled with discussions of theories and opinions, but embracing all that is essential in theory and practice. It is admirably adapted to the wants of the American student. Avoiding all that is uncertain, it presents more clearly to the mind of the reader that which is established and verified by experience. The varied and extensive reading of the author is conspicuously apparent, and all the recent improvements and discoveries in therapeutics and pathology are enucleated in its pages.—*Charleston Med. Journal*.

In the first part of the work the subject of general pathology is presented in outline, giving a beautiful picture of its distinguishing features, and throughout the succeeding chapters we find that he has kept scrupulously within the bounds of sound reasoning and legitimate deduction. Upon the whole, we do not hesitate to pronounce it a superior work in its class, and that Dr. Dickson merits a place in the first rank of American writers.—*Western Lancet*.

DRUITT (ROBERT), M. R. C. S., &c.

THE PRINCIPLES AND PRACTICE OF MODERN SURGERY. Edited by F. W. SARGENT, M. D., author of "Minor Surgery," &c. Illustrated with one hundred and ninety-three wood-engravings. In one very handsomely printed octavo volume, leather, of 576 large pages. \$3 00.

Dr. Drutt's researches into the literature of his subject have been not only extensive, but well directed; the most discordant authors are fairly and impartially quoted, and, while due credit is given to each, their respective merits are weighed with an unprejudiced hand. The grain of wheat is preserved, and the chaff is unmercifully stripped off. The arrangement is simple and philosophical, and the style, though clear and interesting, is so precise, that the book contains more information condensed into a few words than any other surgical work with which we are acquainted.—*London Medical Times and Gazette.*

Drutt's Surgery is too well known to the American medical profession to require its announcement anywhere. Probably no work of the kind has ever been more cordially received and extensively circulated than this. The fact that it comprehends in a comparatively small compass, all the essential ele-

ments of theoretical and practical Surgery—that it is found to contain reliable and authentic information on the nature and treatment of nearly all surgical affections—is a sufficient reason for the liberal patronage it has obtained. The editor, Dr. F. W. Sargent, has contributed much to enhance the value of the work, by such American improvements as are calculated more perfectly to adapt it to our own views and practice in this country. It abounds everywhere with spirited and life-like illustrations, which to the young surgeon, especially, are of no minor consideration. Every medical man frequently needs just such a work as this, for immediate reference in moments of sudden emergency, when he has not time to consult more elaborate treatises.—*The Ohio Medical and Surgical Journal.*

No work, in our opinion, equals it in presenting so much valuable surgical matter in so small a compass.—*St. Louis Med. and Surgical Journal.*

DALTON, JR. (J. C.), M. D.

Professor of Physiology in the College of Physicians, New York.

A TREATISE ON HUMAN PHYSIOLOGY, designed for the use of Students and Practitioners of Medicine. With two hundred and fifty-four illustrations on wood. In one very beautiful octavo volume, of over 600 pages, extra cloth, \$1 00; leather, raised bands, \$4 25. (Now ready, Jan. 1859.)

The object of the author has been to present a condensed view of the present condition of his subject, divested of mere theoretical views and hypothetical reasonings, but comprehending all important details which may be received as definitely settled. His long experience as an investigator and as a teacher has given him peculiar advantages in this, and he has endeavored wherever practicable to show the means by which results have been reached, so as to afford the student the means of pursuing original research, as well as a complete text-book of the science in its most advanced condition. Of the numerous illustrations, all are original with the exception of eleven, so that the whole possesses a completeness and authority not otherwise attainable, and in the mechanical execution every care has been taken to present one of the handsomest volumes as yet produced by the American press.

To our mind, fulfils in a most admirable manner the objects contemplated by the author. The broad field of physiology has been traversed with discrimination, and its most valuable acquisitions com-

pressed into a reasonable compass, embracing likewise the results of recent laborers in this department of our science.—*Med. and Surg. Reporter, Jan. 29, 1859.*

DUNGLISON, FORBES, TWEEDIE, AND CONOLLY.

THE CYCLOPEDIA OF PRACTICAL MEDICINE: comprising Treatises on the Nature and Treatment of Diseases, Materia Medica, and Therapeutics, Diseases of Women and Children, Medical Jurisprudence, &c. &c. In four large super-royal octavo volumes, of 3254 double-columned pages, strongly and handsomely bound, with raised bands. \$12 00.

. This work contains no less than four hundred and eighteen distinct treatises, contributed by sixty-eight distinguished physicians, rendering it a complete library of reference for the country practitioner.

The most complete work on Practical Medicine extant; or, at least, in our language.—*Buffalo Medical and Surgical Journal.*

For reference, it is above all price to every practitioner.—*Western Lancet.*

One of the most valuable medical publications of the day—as a work of reference it is invaluable.—*Western Journal of Medicine and Surgery.*

It has been to us, both as learner and teacher, a work for ready and frequent reference, one in which modern English medicine is exhibited in the most advantageous light.—*Medical Examiner.*

We rejoice that this work is to be placed within the reach of the profession in this country, it being unquestionably one of very great value to the prac-

itioner. This estimate of it has not been formed from a hasty examination, but after an intimate acquaintance derived from frequent consultation of it during the past nine or ten years. The editors are practitioners of established reputation, and the list of contributors embraces many of the most eminent professors and teachers of London, Edinburgh, Dublin, and Glasgow. It is, indeed, the great merit of this work that the principal articles have been furnished by practitioners who have not only devoted especial attention to the diseases about which they have written, but have also enjoyed opportunities for an extensive practical acquaintance with them, and whose reputation carries the assurance of their competency justly to appreciate the opinions of others, while it stamps their own doctrines with high and just authority.—*American Medical Journ.*

DEWEES'S COMPREHENSIVE SYSTEM OF MIDWIFERY. Illustrated by occasional cases and many engravings. Twelfth edition, with the author's last improvements and corrections. In one octavo volume, extra cloth, of 600 pages. \$3 20.

DEWEES'S TREATISE ON THE PHYSICAL AND MEDICAL TREATMENT OF CHILDREN. The last edition. In one volume, octavo, extra cloth, 648 pages. \$2 80.

DEWEES'S TREATISE ON THE DISEASES OF FEMALES. Tenth edition. In one volume, octavo extra cloth, 532 pages, with plates. \$3 00.

DANA ON ZOOPHYTES AND CORALS. In one volume, Imperial quarto, extra cloth, with woodcuts. \$15 00. Also, **AN ATLAS,** in one volume, Imperial folio, with sixty-one magnificent colored plates. Bound in half morocco. \$30 00.

DE LA BECHE'S GEOLOGICAL OBSERVER. In one very large and handsome octavo volume, extra cloth, of 700 pages, with 300 woodcuts. \$4 00.

FRICK ON RENAL AFFECTIONS; their Diagnosis and Pathology. With illustrations. One volume, royal 12mo., extra cloth. 75 cents.

DUNGLISON (ROBLEY), M. D.,

Professor of Institutes of Medicine in the Jefferson Medical College, Philadelphia.

NEW AND ENLARGED EDITION, Now Ready, 1858.

MEDICAL LEXICON; a Dictionary of Medical Science, containing a concise Explanation of the various Subjects and Terms of Anatomy, Physiology, Pathology, Hygiene, Therapeutics, Pharmacology, Pharmacy, Surgery, Obstetrics, Medical Jurisprudence, Dentistry, &c. Notices of Climate and of Mineral Waters; Formulæ for Official, Empirical, and Dietetic Preparations, &c. With French and other Synonyms. FIFTEENTH EDITION, revised and very greatly enlarged. In one very large and handsome octavo volume, of 92 double-columned pages, in small type; strongly bound in leather, with raised bands. Price \$4 00.

Especial care has been devoted in the preparation of this edition to render it in every respect worthy a continuance of the very remarkable favor which it has hitherto enjoyed. The rapid sale of FIFTEEN large editions, and the constantly increasing demand, show that it is regarded by the profession as the standard authority. Stimulated by this fact, the author has endeavored in the present revision to introduce whatever might be necessary "to make it a satisfactory and desirable—if not indispensable—lexicon, in which the student may search without disappointment for every term that has been legitimated in the nomenclature of the science." To accomplish this, large additions have been found requisite, and the extent of the author's labors may be estimated from the fact that about SIX THOUSAND subjects and terms have been introduced throughout, rendering the whole number of definitions about SIXTY THOUSAND, to accommodate which, the number of pages has been increased by nearly a hundred, notwithstanding an enlargement in the size of the page. The medical press, both in this country and in England, has pronounced the work indispensable to all medical students and practitioners, and the present improved edition will not lose that enviable reputation.

The publishers have endeavored to render the mechanical execution worthy of a volume of such universal use in daily reference. The greatest care has been exercised to obtain the typographical accuracy so necessary in a work of the kind. By the small but exceedingly clear type employed, an immense amount of matter is condensed in its thousand ample pages, while the binding will be found strong and durable. With all these improvements and enlargements, the price has been kept at the former very moderate rate, placing it within the reach of all.

This work, the appearance of the fifteenth edition of which, it has become our duty and pleasure to announce, is perhaps the most stupendous monument of labor and erudition in medical literature. One would hardly suppose after constant use of the preceding editions, where we have never failed to find a sufficiently full explanation of every medical term, that in this edition "about six thousand subjects and terms have been added," with a careful revision and correction of the entire work. It is only necessary to announce the advent of this edition to make it occupy the place of the preceding one on the table of every medical man, as it is without doubt the best and most comprehensive work of the kind which has ever appeared.—*Buffalo Med. Journ.*, Jan. 1858.

The work is a monument of patient research, skilful judgment, and vast physical labor, that will perpetuate the name of the author more effectually than any possible device of stone or metal. Dr. Dunglison deserves the thanks not only of the American profession, but of the whole medical world.—*North Am. Medico-Chir. Review*, Jan. 1858.

A Medical Dictionary better adapted for the wants of the profession than any other with which we are acquainted, and of a character which places it far above comparison and competition.—*Am. Journ. Med. Sciences*, Jan. 1858.

We need only say, that the addition of 6,000 new terms, with their accompanying definitions, may be said to constitute a new work, by itself. We have examined the Dictionary attentively, and are most happy to pronounce it unrivalled of its kind. The erudition displayed, and the extraordinary industry which must have been demanded, in its preparation and perfection, redound to the lasting credit of its author, and have furnished us with a volume indispensable at the present day, to all who would find themselves *au niveau* with the highest standards of medical information.—*Boston Medical and Surgical Journal*, Dec. 31, 1857.

Good lexicons and encyclopedic works generally, are the most labor-saving contrivances which literary men enjoy; and the labor which is required to produce them in the perfect manner of this example is something appalling to contemplate. The author

tells us in his preface that he has added about six thousand terms and subjects to this edition, which, before, was considered universally as the best work of the kind in any language.—*Silliman's Journ.*, March, 1858.

He has razed his gigantic structure to the foundations, and remodelled and reconstructed the entire pile. No less than six thousand additional subjects and terms are illustrated and analyzed in this new edition, swelling the grand aggregate to beyond sixty thousand! Thus is placed before the profession a complete and thorough exponent of medical terminology, without rival or possibility of rivalry.—*Nashville Journ. of Med. and Surg.*, Jan. 1858.

It is universally acknowledged, we believe, that this work is incomparably the best and most complete Medical Lexicon in the English language. The amount of labor which the distinguished author has bestowed upon it is truly wonderful, and the learning and research displayed in its preparation are equally remarkable. Comment and commendation are unnecessary, as no one at the present age thinks of purchasing any other Medical Dictionary than this.—*St. Louis Med. and Surg. Journ.*, Jan. 1858.

It is the foundation stone of a good medical library, and should always be included in the first list of books purchased by the medical student.—*Am. Med. Monthly*, Jan. 1858.

A very perfect work of the kind, undoubtedly the most perfect in the English language.—*Med. and Surg. Reporter*, Jan. 1858.

It is now emphatically the Medical Dictionary of the English language, and for it there is no substitute.—*N. H. Med. Journ.*, Jan. 1858.

It is scarcely necessary to remark that any medical library wanting a copy of Dunglison's Lexicon must be imperfect.—*Glas. Lancet*, Jan. 1858.

We have ever considered it the best authority published, and the present edition we may safely say has no equal in the world.—*Peninsular Med. Journ.*, Jan. 1858.

The most complete authority on the subject to be found in any language.—*Va. Med. Journal*, Feb. '58.

BY THE SAME AUTHOR.

THE PRACTICE OF MEDICINE. A Treatise on Special Pathology and Therapeutics. Third Edition. In two large octavo volumes, leather, of 1,500 pages. \$6 25.

DUNGLISON (ROBLEY), M. D.,

Professor of Institutes of Medicine in the Jefferson Medical College, Philadelphia.

HUMAN PHYSIOLOGY. Eighth edition. Thoroughly revised and extensively modified and enlarged, with five hundred and thirty-two illustrations. In two large and handsomely printed octavo volumes, leather, of about 1500 pages. \$7 00.

In revising this work for its eighth appearance, the author has spared no labor to render it worthy a continuance of the very great favor which has been extended to it by the profession. The whole contents have been rearranged, and to a great extent remodelled; the investigations which of late years have been so numerous and so important, have been carefully examined and incorporated, and the work in every respect has been brought up to a level with the present state of the subject. The object of the author has been to render it a concise but comprehensive treatise, containing the whole body of physiological science, to which the student and man of science can at all times refer with the certainty of finding whatever they are in search of, fully presented in all its aspects; and on no former edition has the author bestowed more labor to secure this result.

We believe that it can truly be said, no more complete repertory of facts upon the subject treated, can anywhere be found. The author has, moreover, that enviable tact at description and that facility and ease of expression which render him peculiarly acceptable to the casual, or the studious reader. This faculty, so requisite in setting forth many graver and less attractive subjects, lends additional charms to one always fascinating.—*Boston Med. and Surg. Journal*, Sept. 1856.

The most complete and satisfactory system of Physiology in the English language.—*Amer. Med. Journal*.

The best work of the kind in the English language.—*Silliman's Journal*.

The present edition the author has made a perfect mirror of the science as it is at the present hour. As a work upon physiology proper, the science of the functions performed by the body, the student will find it all he wishes.—*Nashville Journ. of Med.* Sept. 1856.

That he has succeeded, most admirably succeeded in his purpose, is apparent from the appearance of an eighth edition. It is now the great encyclopaedia on the subject, and worthy of a place in every physician's library.—*Western Lancet*, Sept. 1856.

BY THE SAME AUTHOR. (*Now Ready.*)

GENERAL THERAPEUTICS AND MATERIA MEDICA; adapted for a Medical Text-book. With Indexes of Remedies and of Diseases and their Remedies. SIXTH EDITION, revised and improved. With one hundred and ninety-three illustrations. In two large and handsomely printed octavo vols., leather, of about 1100 pages. \$6 00.

From the Author's Preface.

"Another edition of this work being called for, the author has subjected it to a thorough and careful revision. It has been gratifying to him that it has been found so extensively useful by those for whom it was especially intended, as to require that a sixth edition should be issued in so short a time after the publication of a fifth. Grateful for the favorable reception of the work by the profession, he has bestowed on the preparation of the present edition all those cares which were demanded by the former editions, and has spared no pains to render it a faithful epitome of General Therapeutics and Materia Medica. The copious Indexes of Remedies and of Diseases and their Remedies cannot fail, the author conceives, to add materially to the value of the work."

This work is too widely and too favorably known to require more than the assurance that the author has revised it with his customary industry, introducing whatever has been found necessary to bring it on a level with the most advanced condition of the subject. The number of illustrations has been somewhat enlarged, and the mechanical execution of the volumes will be found to have undergone a decided improvement.

In announcing a new edition of Dr. Dunglison's General Therapeutics and Materia Medica, we have no words of commendation to bestow upon a work whose merits have been heretofore so often and so justly extolled. It must not be supposed, however, that the present is a mere reprint of the previous edition; the character of the author for laborious research, judicious analysis, and clearness of expression, is fully sustained by the numerous additions he has made to the work, and the careful revision to which he has subjected the whole.—*N. A. Medico-Chir. Review*, Jan. 1858.

The work will, we have little doubt, be bought and read by the majority of medical students; its size, arrangement, and reliability recommend it to all; no one, we venture to predict, will study it without profit, and there are few to whom it will not be in some measure useful as a work of reference. The young practitioner, more especially, will find the copious indexes appended to this edition of great assistance in the selection and preparation of suitable formulæ.—*Charleston Med. Journ. and Review*, Jan. 1858.

BY THE SAME AUTHOR. (*A new Edition.*)

NEW REMEDIES, WITH FORMULÆ FOR THEIR PREPARATION AND ADMINISTRATION. Seventh edition, with extensive Additions. In one very large octavo volume, leather, of 770 pages. \$3 75.

Another edition of the "New Remedies" having been called for, the author has endeavored to add everything of moment that has appeared since the publication of the last edition.

The articles treated of in the former editions will be found to have undergone considerable expansion in this, in order that the author might be enabled to introduce, as far as practicable, the results of the subsequent experience of others, as well as of his own observation and reflection; and to make the work still more deserving of the extended circulation with which the preceding editions have been favored by the profession. By an enlargement of the page, the numerous additions have been incorporated without greatly increasing the bulk of the volume.—*Profusus*.

One of the most useful of the author's works.—*Southern Medical and Surgical Journal*.

This elaborate and useful volume should be found in every medical library, for as a book of reference, for physicians, it is unsurpassed by any other work in existence, and the double index for diseases and for remedies, will be found greatly to enhance its value.—*New York Med. Gazette*.

The great learning of the author, and his remarkable industry in pushing his researches into every source whence information is derivable, have enabled him to throw together an extensive mass of facts and statements, accompanied by full reference to authorities; which last feature renders the work practically valuable to investigators who desire to examine the original papers.—*The American Journal of Pharmacy*.

ERICHSEN (JOHN),
Professor of Surgery in University College, London, &c.

THE SCIENCE AND ART OF SURGERY; BEING A TREATISE ON SURGICAL INJURIES, DISEASES, AND OPERATIONS. New and improved American, from the second enlarged and carefully revised London edition. Illustrated with over four hundred engravings on wood. In one large and handsome octavo volume, of one thousand closely printed pages, leather raised bands. \$4 50. (*Now Ready, January, 1859.*)

The very distinguished favor with which this work has been received on both sides of the Atlantic has stimulated the author to render it even more worthy of the position which it has so rapidly attained as a standard authority. Every portion has been carefully revised, numerous additions have been made, and the most watchful care has been exercised to render it a complete exponent of the most advanced condition of surgical science. In this manner the work has been enlarged by about a hundred pages, while the series of engravings has been increased by more than a hundred, rendering it one of the most thoroughly illustrated volumes before the profession. The additions of the author having rendered unnecessary most of the notes of the former American editor, but little has been added in this country; some few notes and occasional illustrations have, however, been introduced to elucidate American modes of practice.

It is, in our humble judgment, decidedly the best book of the kind in the English language. Strange that just such books are not oftener produced by public teachers of surgery in this country and Great Britain. Indeed, it is a matter of great astonishment, but no less true than astonishing, that of the many works on surgery republished in this country within the last fifteen or twenty years as text-books for medical students, this is the only one that even approximates to the fulfilment of the peculiar wants of young men just entering upon the study of this branch of the profession.—*Western Jour. of Med. and Surgery.*

Its value is greatly enhanced by a very copious well-arranged index. We regard this as one of the most valuable contributions to modern surgery. To one entering his novitiate of practice, we regard it the most serviceable guide which he can consult. He will find a fulness of detail leading him through every step of the operation, and not deserting him until the final issue of the case is decided. For the same reason we recommend it to those whose routine of practice lies in such parts of the country that they must

rarely encounter cases requiring surgical management.—*Stethoscope.*

Embracing, as will be perceived, the whole surgical domain, and each division of itself almost complete and perfect, each chapter full and explicit, each subject faithfully exhibited, we can only express our estimate of it in the aggregate. We consider it an excellent contribution to surgery, as probably the best single volume now extant on the subject, and with great pleasure we add it to our text-books.—*Nashville Journal of Medicine and Surgery.*

Prof. Erichsen's work, for its size, has not been surpassed; his nine hundred and eight pages, profusely illustrated, are rich in physiological, pathological, and operative suggestions; doctrines, details and processes; and will prove a reliable resource for information, both to physician and surgeon, in the hour of peril.—*N. O. Med. and Surg. Journal.*

We are acquainted with no other work which so much good sense, sound principle, and practical inferences, stamp every page.—*American Lanet.*

ELLIS (BENJAMIN), M. D.

THE MEDICAL FORMULARY: being a Collection of Prescriptions, derived from the writings and practice of many of the most eminent physicians of America and Europe. Together with the usual Dietetic Preparations and Antidotes for Poisons. To which is added an Appendix, on the Endermic use of Medicines, and on the use of Ether and Chloroform. The whole accompanied with a few brief Pharmaceutic and Medical Observations. Tenth edition, revised and much extended by ROBERT P. THOMAS, M. D., Professor of Materia Medica in the Philadelphia College of Pharmacy. In one neat octavo volume, extra cloth, of 296 pages. \$1 75

FOWNES (GEORGE), PH. D., &c.

ELEMENTARY CHEMISTRY; Theoretical and Practical. With numerous illustrations. Edited, with Additions, by ROBERT BRIDGES, M. D. In one large royal 12mo. volume, of over 550 pages, with 181 wood-cuts. In leather, \$1 50; extra cloth, \$1 35.

We know of no better text-book, especially in the difficult department of organic chemistry, upon which it is particularly full and satisfactory. We would recommend it to preceptors as a capital "office book" for their students who are beginners in Chemistry. It is copiously illustrated with excellent wood-cuts, and altogether admirably "got up."—*N. J. Medical Reporter.*

A standard manual, which has long enjoyed the reputation of embodying much knowledge in a small space. The author has achieved the difficult task of condensation with masterly tact. His book is concise without being dry, and brief without being too dogmatical or general.—*Virginia Med. and Surgical Journal.*

The work of Dr. Fownes has long been before the public, and its merits have been fully appreciated as the best text-book on chemistry now in existence. We do not, of course, place it in a rank superior to the works of Brande, Graham, Turner, Gregory, or Gmelin, but we say that, as a work for students, it is preferable to any of them.—*London Journal of Medicine.*

A work well adapted to the wants of the student. It is an excellent exposition of the chief doctrines and facts of modern chemistry. The size of the work, and still more the condensed yet perspicuous style in which it is written, abolve it from the charges very properly urged against most manuals termed popular.—*Edinburgh Journal of Medical Science.*

FISKE FUND PRIZE ESSAYS.

THE EFFECTS OF CLIMATE ON TUBERCULOUS DISEASE. By EDWIN LEE, M. R. C. S. London, and **THE INFLUENCE OF PREGNANCY ON THE DEVELOPMENT OF TUBERCLES.** By EDWARD WARREN, M. D., of Edenton, N. C. Together in one neat octavo volume, extra cloth. \$1 00. (*Just Ready.*)

FERGUSSON (WILLIAM), F. R. S.,
Professor of Surgery in King's College, London, &c.

A SYSTEM OF PRACTICAL SURGERY. Fourth American, from the third and enlarged London edition. In one large and beautifully printed octavo volume, of about 700 pages, with 393 handsome illustrations, leather. \$3 00.

No work was ever written which more nearly comprehended the necessities of the student and practitioner, and was more carefully arranged to that single purpose than this.—*N. Y. Med. Journal.*

The addition of many new pages makes this work more than ever indispensable to the student and practitioner.—*Ranking's Abstract.*

FLINT (AUSTIN), M. D.,

Professor of the Theory and Practice of Medicine in the University of Louisville, &c.

(An Important New Work.)

PHYSICAL EXPLORATION AND DIAGNOSIS OF DISEASES AFFECTING THE RESPIRATORY ORGANS. In one large and handsome octavo volume, extra cloth, 636 pages. \$3 00.

We can only state our general impression of the high value of this work, and cordially recommend it to all. We regard it, in point both of arrangement and of the marked ability of its treatment of the subjects, as destined to take the first rank in works of this class. So far as our information extends, it has at present no equal. To the practitioner, as well as the student, it will be invaluable in clearing up the diagnosis of doubtful cases, and in shedding light upon difficult phenomena.—*Buffalo Med. Journal.*

This is the most elaborate work devoted exclusively to the physical exploration of diseases of the

lungs, with which we are acquainted in the English language.—*Boston Med. and Surg. Journal.*

A work of original observation of the highest merit. We recommend the treatise to every one who wishes to become a correct auscultator. Based to a very large extent upon cases numerically examined, it carries the evidence of careful study and discrimination upon every page. It does credit to the author, and, through him, to the profession in this country. It is, what we cannot call every book upon auscultation, a readable book.—*Am. Jour. Med. Sciences.*

NOW COMPLETE,

GRAHAM (THOMAS), F. R. S.,

THE ELEMENTS OF INORGANIC CHEMISTRY, including the Applications of the Science in the Arts. New and much enlarged edition, by HENRY WATTS and ROBERT BRIDGES, M. D. Complete in one large and handsome octavo volume, of over 800 very large pages, with two hundred and thirty-two wood-cuts, extra cloth. \$4 00.

Part II., completing the work from p. 431 to end, with Index, Title Matter, &c., may be had separate, cloth backs and paper sides. Price \$2 50.

The long delay which has intervened since the appearance of the first portion of this work, has rendered necessary an Appendix, embodying the numerous and important investigations and discoveries of the last few years in the subjects contained in Part I. This occupies a large portion of Part II., and will be found to present a complete abstract of the most recent researches in the general principles of the science, as well as all details necessary to bring the whole work thoroughly up to the present time in all departments of Inorganic Chemistry.

Gentlemen desirous of completing their copies of the work are requested to apply for Part II. without delay. It will be sent by mail, prepaid, on receipt of the amount, \$2 50.

It is a very acceptable addition to the library of standard books of every chemical student. No reader of English works on this science can afford to be without this edition of Prof. Graham's Elements.—*Baltimore Journal*, March, 1858.

From Prof. J. L. Cravocour, New Orleans School of Medicine, May 9, 1858.

It is beyond all question the best systematic work on Chemistry in the English language, and I am gratified to find that an American edition at a moderate price has been issued, so as to place it within the means of students. It will be the only text-book I shall now recommend to my class.

From Prof. Wolcott Gibbs, N. Y. Free Academy, May 25, 1858.

The work is an admirable one in all respects, and its republication here cannot fail to exert a positive influence upon the progress of science in this country.

From Prof. E. N. Horsford, Harvard College, April 27, 1858.

It has, in its earlier and less perfect editions, been familiar to me, and the excellence of its plan and the clearness and completeness of its discussions, have long been my admiration.

GRIFFITH (ROBERT E.), M. D., &c.

A UNIVERSAL FORMULARY, containing the methods of Preparing and Administering Official and other Medicines. The whole adapted to Physicians and Pharmacoeutists. SECOND EDITION, thoroughly revised, with numerous additions, by ROBERT P. THOMAS, M. D., Professor of Materia Medica in the Philadelphia College of Pharmacy. In one large and handsome octavo volume, extra cloth, of 650 pages, double columns. \$3 00; or bound in sheep, \$3 25.

It was a work requiring much perseverance, and when published was looked upon as by far the best work of its kind that had issued from the American press. Prof. Thomas has certainly "improved," as well as added to this Formulary, and has rendered it additionally deserving of the confidence of pharmacoeutists and physicians.—*Am. Journal of Pharmacy.*

We are happy to announce a new and improved edition of this, one of the most valuable and useful works that have emanated from an American pen. It would do credit to any country, and will be found of daily usefulness to practitioners of medicine; it is better adapted to their purposes than the dispensatories.—*Southern Med. and Surg. Journal.*

It is one of the most useful books a country practitioner can possibly have in his possession.—*Medical Chronicle.*

This is a work of six hundred and fifty-one pages, embracing all on the subject of preparing and admin-

istering medicines that can be desired by the physician and pharmacoeutist.—*Western Lancet.*

The amount of useful, every-day matter for a practicing physician, is really immense.—*Boston Med. and Surg. Journal.*

We predict a great sale for this work, and we especially recommend it to all medical teachers.—*Richmond Steethoscope.*

This edition of Dr. Griffith's work has been greatly improved by the revision and ample additions of Dr. Thomas, and is now, we believe, one of the most complete works of its kind in any language. The additions amount to about seventy pages, and no effort has been spared to include in them all the recent improvements which have been published in medical journals, and systematic treatises. A work of this kind appears to us indispensable to the physician, and there is none we can more cordially recommend.—*N. Y. Journal of Medicine.*

GLUGE (GOTTLIEB), M. D.,

Professor of Physiology and Pathological Anatomy in the University of Brussels, &c.

AN ATLAS OF PATHOLOGICAL HISTOLOGY. Translated, with Notes and Additions, by JOSEPH LEDY, M. D., Professor of Anatomy in the University of Pennsylvania. In one volume, very large imperial quarto, extra cloth, with 320 figures, plain and colored, on twelve copperplates. \$5 00.

GROSS (SAMUEL D.), M. D.,
Professor of Surgery in the Jefferson Medical College of Philadelphia, &c.

New Edition (Now Ready.)

ELEMENTS OF PATHOLOGICAL ANATOMY. Third edition, thoroughly revised and greatly improved. In one large and very handsome octavo volume, with about three hundred and fifty beautiful illustrations, of which a large number are from original drawings. Price in extra cloth, \$4 75; leather, raised bands, \$5 25.

The very rapid advances in the Science of Pathological Anatomy during the last few years have rendered essential a thorough modification of this work, with a view of making it a correct exponent of the present state of the subject. The very careful manner in which this task has been executed, and the amount of alteration which it has undergone, have enabled the author to say that "with the many changes and improvements now introduced, the work may be regarded almost as a new treatise," while the efforts of the author have been seconded as regards the mechanical execution of the volume, rendering it one of the handsomest productions of the American press. A very large number of new and beautiful original illustrations have been introduced, and the work, it is hoped, will fully maintain the reputation hitherto enjoyed by it of a complete and practical exposition of its difficult and important subject.

We most sincerely congratulate the author on the successful manner in which he has accomplished his proposed object. His book is most admirably calculated to fill up a blank which has long been felt to exist in this department of medical literature, and as such must become very widely circulated amongst all classes of the profession.—*Dublin Quarterly Journ. of Med. Science*, Nov. 1857.

We have been favorably impressed with the general manner in which Dr. Gross has executed his task of affording a comprehensive digest of the present state of the literature of Pathological Anatomy, and have much pleasure in recommending his work to our readers, as we believe one well deserving of diligent perusal and careful study.—*Montreal Med. Chron.*, Sept. 1857.

BY THE SAME AUTHOR.

A PRACTICAL TREATISE ON THE DISEASES, INJURIES, AND MALFORMATIONS OF THE URINARY BLADDER, THE PROSTATE GLAND, AND THE URETHRA. Second Edition, revised and much enlarged, with one hundred and eighty-four illustrations. In one large and very handsome octavo volume, of over nine hundred pages. In leather, raised bands, \$5 25; extra cloth, \$4 75.

A volume replete with truths and principles of the utmost value in the investigation of these diseases.—*American Medical Journal*.

On the appearance of the first edition of this work, the leading English medical review predicted that it would have a "permanent place in the literature of surgery worthy to rank with the best works of the present age." This prediction has been amply fulfilled. Dr. Gross's treatise has been found to supply completely the want which has been felt ever since the elevation of surgery to the rank of a science, of a good practical treatise on the diseases of the bladder and its accessory organs. Philosophical in its design, methodical in its arrangement, ample and

sound in its practical details, it may in truth be said to leave scarcely anything to be desired on so important a subject, and with the additions and modifications resulting from future discoveries and improvements, it will probably remain one of the most valuable works on this subject so long as the science of medicine shall exist.—*Boston Med. and Surg. Journal*.

Whoever will peruse the vast amount of valuable practical information it contains, and which we have been unable even to notice, will, we think, agree with us, that there is no work in the English language which can make any just pretensions to be its equal.—*N. Y. Journal of Medicine*.

BY THE SAME AUTHOR.

A PRACTICAL TREATISE ON FOREIGN BODIES IN THE AIR-PASSESAGES. In one handsome octavo volume, extra cloth, with illustrations. pp. 468. \$2 75.

BY THE SAME AUTHOR. (In press.)

A SYSTEM OF SURGERY; Diagnostic, Pathological, Therapeutic, and Operative. With very numerous engravings on wood. In two large octavo volumes.

GIBSON (WILLIAM), M. D.,

Late Professor of Surgery in the University of Pennsylvania, &c

INSTITUTES AND PRACTICE OF SURGERY; being Outlines of a Course of Lectures. Eighth edition, improved and altered. With thirty-four plates. In two handsome octavo volumes, containing about 1000 pages, leather, raised bands. \$6 50.

GRAY (HENRY), F. R. S.,

Lecturer on Anatomy at St. George's Hospital, London, &c.

ANATOMY, DESCRIPTIVE AND SURGICAL. The Drawings by H. V. CARTER, M. D., late Demonstrator on Anatomy at St. George's Hospital; the Dissections jointly by the AUTHOR and Dr. CARTER. In one magnificent imperial octavo volume, with 325 large and elaborate engravings on wood. (*At press.*)

The author has endeavored in this work to cover a more extended range of subjects than is customary in the ordinary text-books, by giving not only the details necessary for the student, but also the application of those details in the practice of medicine and surgery, thus rendering it not only a guide for the learner, but an admirable work of reference for the active practitioner. The engravings form a special feature in the work, many of them being the size of nature, nearly all original, and having the names of the various parts printed on the body of the cut, in place of figures of reference with descriptions at the foot. They thus form a complete and splendid series, which will greatly assist the student in obtaining a clear idea of Anatomy, and will also serve to refresh the memory of those who may find in the exigencies of practice the necessity of recalling the details of the dissecting room.

GARDNER'S MEDICAL CHEMISTRY, for the use of Students and the Profession. In one royal 12mo. vol., ex. cloth, pp. 306, with illustrations. \$1 00.

HUGHES' CLINICAL INTRODUCTION TO

THE PRACTICE OF AUSCULTATION AND OTHER MODES OF PHYSICAL DIAGNOSIS, IN DISEASES OF THE LUNGS AND HEART. Second American, from the second London edition. 1 vol. royal 12mo., ex. cloth, pp. 304. \$1 00.

HOBLYN (RICHARD D.), M. D.

A DICTIONARY OF THE TERMS USED IN MEDICINE AND THE COLLATERAL SCIENCES. A new American edition. Revised, with numerous Additions, by ISAAC HAYS, M. D., editor of the "American Journal of the Medical Sciences." In one large royal 12mo. volume, leather, of over 500 double columned pages. \$1 50.

If the frequency with which we have referred to this volume since its reception from the publisher, two or three weeks ago, be any criterion for the future, the binding will soon have to be renewed, even with careful handling. We find that Dr. Hays has done the profession great service by his careful and industrious labors. The Dictionary has thus become eminently suited to our medical brethren in this country. The additions by Dr. Hays are in brackets, and we believe there is not a single page but bears these insignia; in every instance which we have thus far noticed, the additions are really needed and exceedingly valuable. We heartily commend the work to all who wish to be as correct in medical terminology.—*Boston Med. and Surg. Journal.*

To both practitioner and student, we recommend this dictionary as being convenient in size, accurate in definition, and sufficiently full and complete for ordinary consultation.—*Charleston Med. Journ. and Review.*

Hoblyn has always been a favorite dictionary, and in its present enlarged and improved form will give greater satisfaction than ever. The American editor, Dr. Hays, has made many very valuable additions.—*N. J. Med. Reporter.*

To supply the want of the medical reader arising from this cause, we know of no dictionary better arranged and adapted than the one bearing the above title. It is not encumbered with the obsolete terms of a bygone age, but it contains all that are now in use; embracing every department of medical science down to the very latest date. The volume is of a convenient size to be used by the medical student, and yet large enough to make a respectable appearance in the library of a physician.—*Western Lancet.*

Hoblyn's Dictionary has long been a favorite with us. It is the best book of definitions we have, and ought always to be upon the student's table.—*Southern Med. and Surg. Journal.*

HUNTER (JOHN).

(See "Ricord," page 26, for Ricord's edition of Hunter on Venereal.)

HOLLAND (SIR HENRY), BART., M. D., F. R. S.,

Physician in Ordinary to the Queen of England, &c.

MEDICAL NOTES AND REFLECTIONS. From the third London edition. In one handsome octavo volume, extra cloth. \$3 00.

HABERSHON (S. O.), M. D.,

Assistant Physician to and Lecturer on Materia Medica and Therapeutics at Guy's Hospital, &c.

PATHOLOGICAL AND PRACTICAL OBSERVATIONS ON DISEASES OF THE ALIMENTARY CANAL, OESOPHAGUS, STOMACH, CÆCUM, AND INTESTINES. With illustrations on wood. In one handsome octavo volume. (*Publishing in the Medical News and Library for 1858 and 1859.*)

HORNER (WILLIAM E.), M. D.,

Professor of Anatomy in the University of Pennsylvania.

SPECIAL ANATOMY AND HISTOLOGY. Eighth edition. Extensively revised and modified. In two large octavo volumes, extra cloth, of more than one thousand pages, handsomely printed, with over three hundred illustrations. \$6 00.

BY THE SAME AUTHOR.

ANATOMICAL ATLAS. By Professors HORNER and SMITH. See Smith, page 28.

HAMILTON (FRANK H.), M. D.,

Professor of Surgery, in Buffalo Medical College, &c.

A COMPLETE TREATISE ON FRACTURES AND DISLOCATIONS. In one handsome octavo volume, with several hundred illustrations. (*Preparing.*)

JONES (T. WHARTON), F. R. S.,

Professor of Ophthalmic Medicine and Surgery in University College, London, &c.

THE PRINCIPLES AND PRACTICE OF OPHTHALMIC MEDICINE AND SURGERY. With one hundred and ten illustrations. Second American from the second and revised London edition, with additions by EDWARD HARTSHORN, M. D., Surgeon to Wills' Hospital, &c. In one large, handsome royal 12mo. volume, extra cloth, of 500 pages. \$1 50.

We are confident that the reader will find, on perusal, that the execution of the work amply fulfils the promise of the preface, and sustains, in every point, the already high reputation of the author as an ophthalmic surgeon as well as a physiologist and pathologist. The book is evidently the result of much labor and research, and has been written with the greatest care and attention; it possesses that best quality which a general work, like a system or manual can show, viz: the quality of having all the materials whencesoever derived, so thorough-

ly wrought up, and digested in the author's mind, as to come forth with the freshness and impressiveness of an original production. We entertain little doubt that this book will become what its author hoped it might become, a manual for daily reference and consultation by the student and the general practitioner. The work is marked by that correctness, clearness, and precision of style which distinguish all the productions of the learned author.—*British and For. Med. Review.*

JONES (C. HANDFIELD), F. R. S., & EDWARD H. SIEVEKING, M. D.,
Assistant Physicians and Lecturers in St. Mary's Hospital, London.

A MANUAL OF PATHOLOGICAL ANATOMY. First American Edition, Revised. With three hundred and ninety-seven handsome wood engravings. In one large and beautiful octavo volume of nearly 750 pages, leather. \$3 75.

As a concise text-book, containing, in a condensed form, a complete outline of what is known in the domain of Pathological Anatomy, it is perhaps the best work in the English language. Its great merit consists in its completeness and brevity, and in this respect it supplies a great desideratum in our literature. Heretofore the student of pathology was obliged to glean from a great number of monographs, and the field was so extensive that but few cultivated it with any degree of success. As a simple work of reference, therefore, it is of great value to the student of pathological anatomy, and should be in every physician's library.—*Western Lancet*.

In offering the above titled work to the public, the authors have not attempted to intrude new views on their professional brethren, but simply to lay before them, what has long been wanted, an outline of the

present condition of pathological anatomy. In this they have been completely successful. The work is one of the best compilations which we have ever perused.—*Charleston Medical Journal and Review*.

We urge upon our readers and the profession generally the importance of informing themselves in regard to modern views of pathology, and recommend to them to procure the work before us as the best means of obtaining this information.—*Stethoscope*.

From the casual examination we have given we are inclined to regard it as a text-book, plain, rational, and intelligible, such a book as the practical man needs for daily reference. For this reason it will be likely to be largely useful, as it suits itself to those busy men who have little time for minute investigation, and prefer a summary to an elaborate treatise.—*Buffalo Medical Journal*.

KIRKES (WILLIAM SENHOUSE), M. D.,

Demonstrator of Morbid Anatomy at St. Bartholomew's Hospital, &c.

A MANUAL OF PHYSIOLOGY. A new American, from the third and improved London edition. With two hundred illustrations. In one large and handsome royal 12mo. volume, leather. pp. 596. \$2 00. (*Just Issued, 1857.*)

In again passing this work through his hands, the author has endeavored to render it a correct exposition of the present condition of the science, making such alterations and additions as have been dictated by further experience, or as the progress of investigation has rendered desirable. In every point of mechanical execution the publishers have sought to make it superior to former editions, and at the very low price at which it is offered, it will be found one of the handsomest and cheapest volumes before the profession.

In making these improvements, care has been exercised not unduly to increase its size, thus maintaining its distinctive characteristic of presenting within a moderate compass a clear and connected view of its subjects, sufficient for the wants of the student.

This is a new and very much improved edition of Dr. Kirkes' well-known Handbook of Physiology. Originally constructed on the basis of the admirable treatise of Muller, it has in successive editions developed itself into an almost original work, though no change has been made in the plan or arrangement. It combines conciseness with completeness, and is, therefore, admirably adapted for consultation by the busy practitioner.—*Dublin Quarterly Journal*, Feb. 1857.

Its excellence is in its compactness, its clearness, and its carefully cited authorities. It is the most convenient of text-books. These gentlemen, Messrs Kirkes and Paget, have really an immense talent for silence, which is not so common or so cheap as prating people fancy. They have the gift of telling us what we want to know, without thinking it necessary to tell us all they know.—*Boston Med. and Surg. Journal*, May 14, 1857.

One of the very best handbooks of Physiology we possess—presenting just such an outline of the science, comprising an account of its leading facts and generally admitted principles, as the student requires during his attendance upon a course of lectures, or for reference whilst preparing for examination.—*Am. Medical Journal*.

We need only say, that, without entering into discussions of unsettled questions, it contains all the recent improvements in this department of medical science. For the student beginning this study, and the practitioner who has but leisure to refresh his memory, this book is invaluable, as it contains all that is important to know, without special details, which are read with interest only by those who would make a specialty, or desire to possess a critical knowledge of the subject.—*Charleston Medical Journal*.

KNAPP'S TECHNOLOGY; or, Chemistry applied to the Arts and to Manufactures. Edited, with numerous Notes and Additions, by Dr. EDMUND RONALDS and Dr. THOMAS RICHARDSON. First

American edition, with Notes and Additions, by Prof. WALTER R. JOHNSON. In two handsome octavo volumes, extra cloth, with about 500 wood- engravings. \$6 00.

LUDLOW (J. L.), M. D.

A MANUAL OF EXAMINATIONS upon Anatomy, Physiology, Surgery, Practice of Medicine, Obstetrics, Materia Medica, Chemistry, Pharmacy, and Therapeutics. To which is added a Medical Formulary. Designed for Students of Medicine throughout the United States. Third edition, thoroughly revised and greatly extended and enlarged. With three hundred and seventy illustrations. In one large and handsome royal 12mo. volume, leather, of over 800 closely printed pages (*Just Issued.*) \$2 50.

The great popularity of this volume, and the numerous demands for it during the two years in which it has been out of print, have induced the author in its revision to spare no pains to render it a correct and accurate digest of the most recent condition of all the branches of medical science. In many respects it may, therefore, be regarded rather as a new book than a new edition, an entire section on Physiology having been added, as also one on Organic Chemistry, and many portions having been rewritten. A very complete series of illustrations has been introduced, and every care has been taken in the mechanical execution to render it a convenient and satisfactory book for study or reference.

The arrangement of the volume in the form of question and answer renders it especially suited for the office examination of students and for those preparing for graduation.

We know of no better companion for the student during the hours spent in the lecture room, or to refresh, at a glance, his memory of the various topics

crammed into his head by the various professors to whom he is compelled to listen.—*Western Lancet*, May, 1857.

LEHMANN (C. G.)

PHYSIOLOGICAL CHEMISTRY. Translated from the second edition by GEORGE E. DAY, M. D., F. R. S., &c., edited by R. E. ROGERS, M. D., Professor of Chemistry in the Medical Department of the University of Pennsylvania, with illustrations selected from Funke's Atlas of Physiological Chemistry, and an Appendix of plates. Complete in two large and handsome octavo volumes, extra cloth, containing 1200 pages, with nearly two hundred illustrations. \$6 00.

This great work, universally acknowledged as the most complete and authoritative exposition of the principles and details of Zoochemistry, in its passage through the press, has received from Professor Rogers such care as was necessary to present it in a correct and reliable form. To such a work additions were deemed superfluous, but several years having elapsed between the appearance in Germany of the first and last volume, the latter contained a supplement, embodying numerous corrections and additions resulting from the advance of the science. These have all been incorporated in the text in their appropriate places, while the subjects have been still further elucidated by the insertion of illustrations from the Atlas of Dr. Otto Funke. With the view of supplying the student with the means of convenient comparison, a large number of wood-cuts, from works on kindred subjects, have also been added in the form of an Appendix of Plates. The work is, therefore, presented as in every way worthy the attention of all who desire to be familiar with the modern facts and doctrines of Physiological Science.

The most important contribution as yet made to Physiological Chemistry.—*Am. Journal Med. Sciences*, Jan. 1856.

The present volumes belong to the small class of medical literature which comprises elaborate works of the highest order of merit.—*Montreal Med. Chronicle*, Jan. 1856.

The work of Lehmann stands unrivalled as the most comprehensive book of reference and information extant on every branch of the subject on which

it treats.—*Edinburgh Monthly Journal of Medical Science*.

Already well known and appreciated by the scientific world, Professor Lehmann's great work requires no laudatory sentences, as, under a new garb, it is now presented to us. The little space at our command would ill suffice to set forth even a small portion of its excellences.—*Boston Med. and Surg. Journal*, Dec. 1856.

BY THE SAME AUTHOR. (*Just Issued.*)

MANUAL OF CHEMICAL PHYSIOLOGY. Translated from the German, with Notes and Additions, by J. CHESTON MORRIS, M. D., with an Introductory Essay on Vital Force, by SAMUEL JACKSON, M. D., Professor of the Institutes of Medicine in the University of Pennsylvania. With illustrations on wood. In one very handsome octavo volume, extra cloth, of 336 pages. \$2 25.

From Prof. Jackson's Introductory Essay.

In adopting the handbook of Dr. Lehmann as a manual of Organic Chemistry for the use of the students of the University, and in recommending his original work of PHYSIOLOGICAL CHEMISTRY for their more mature studies, the high value of his researches, and the great weight of his authority in that important department of medical science are fully recognized.

LAWRENCE (W.), F. R. S., &c.

A TREATISE ON DISEASES OF THE EYE. A new edition, edited, with numerous additions, and 243 illustrations, by ISAAC HAYS, M. D., Surgeon to Will's Hospital, &c. In one very large and handsome octavo volume, of 950 pages, strongly bound in leather with raised bands. \$5 00.

This admirable treatise—the safest guide and most comprehensive work of reference, which is within the reach of the profession.—*Statistoscope*.

This standard text-book on the department of which it treats, has not been superseded, by any or all of the numerous publications on the subject heretofore issued. Nor with the multiplied improvements of Dr. Hays, the American editor, is it at all

likely that this great work will cease to merit the confidence and preference of students or practitioners. Its ample extent—nearly one thousand large octavo pages—has enabled both author and editor to do justice to all the details of this subject, and condense in this single volume the present state of our knowledge of the whole science in this department, whereby its practical value cannot be excelled.—*N. Y. Med. Gaz.*

LAYCOCK (THOMAS), M. D., F. R. S. E.,

Professor of Practical and Clinical Medicine in the University of Edinburgh, &c.

LECTURES ON THE PRINCIPLES AND METHODS OF MEDICAL OBSERVATION AND RESEARCH. For the Use of Advanced Students and Junior Practitioners. In one very neat royal 12mo. volume, extra cloth. Price \$1 00.

LALLEMAND AND WILSON.

A PRACTICAL TREATISE ON THE CAUSES, SYMPTOMS, AND TREATMENT OF SPERMATORRHOEA. By M. LALLEMAND. Translated and edited by HENRY J. McDOUGALL. Third American edition. To which is added—ON DISEASES OF THE VESICULÆ SEMINALES; AND THEIR ASSOCIATED ORGANS. With special reference to the Morbid Secretions of the Prostatic and Urethral Mucous Membrane. By MARRIS WILSON, M. D. In one neat octavo volume, of about 400 pp., extra cloth. \$2 00. (*Now Ready.*)

Although the views of M. Lallemand on Spermatorrhœa have unquestionably exercised a very great influence, and the treatment advocated by him has been very generally adopted, still, a number of years having elapsed since his work was given to the world, the publishers have thought that the value of the present edition would be enhanced by the addition of the little treatise of Dr. MARRIS WILSON. In it the causes of the different varieties of Spermatorrhœa are investigated with the aid of modern pathology, from which, combined with the most recent experience of the profession, the attempt is made to deduce a rational system of curative treatment. Whatever deficiencies may have been caused in the work of M. Lallemand by the progress of medical science, will, it is hoped, be in this manner supplied.

LA ROCHE (R.), M. D., &c.

YELLOW FEVER, considered in its Historical, Pathological, Etiological, and Therapeutical Relations. Including a Sketch of the Disease as it has occurred in Philadelphia from 1699 to 1854, with an examination of the connections between it and the fevers known under the same name in other parts of temperate as well as in tropical regions. In two large and handsome octavo volumes of nearly 1500 pages, extra cloth. \$7 00.

From Professor S. H. Dickson, Charleston, S. C.,
September 18, 1855.

A monument of intelligent and well applied research, almost without example. It is, indeed, in itself, a large library, and is destined to constitute the special resort as a book of reference, in the subject of which it treats, to all future time.

We have not time at present, engaged as we are, by day and by night, in the work of combating this very disease, now prevailing in our city, to do more than give this cursory notice of what we consider as undoubtedly the most able and erudite medical publication our country has yet produced. But in view of the startling fact, that this, the most malignant and unmanageable disease of modern times, has for several years been prevailing in our country to a greater extent than ever before; that it is no longer confined to either large or small cities, but penetrates country villages, plantations, and farm-houses; that it is treated with scarcely better success now than thirty or forty years ago; that there is vast mischief done by ignorant pretenders to knowledge in regard to the disease, and in view of the probability that a majority of southern physicians will be called upon to treat the disease, we trust that this able and comprehensive treatise will be very generally read in the south.—*Memphis Med. Recorder*.

This is decidedly the great American medical work of the day—a full, complete, and systematic treatise, unequalled by any other upon the all-important subject of Yellow Fever. The laborious, indefatigable, and learned author has devoted to it many years of

arduous research and careful study, and the result is such as will reflect the highest honor upon the author and our country.—*Southern Med. and Surg. Journal*.

The genius and scholarship of this great physician could not have been better employed than in the erection of this towering monument to his own fame, and to the glory of the medical literature of his own country. It is destined to remain the great authority upon the subject of Yellow Fever. The student and physician will find in these volumes a résumé of the sum total of the knowledge of the world upon the awful scourge which they so elaborately discuss. The style is so soft and so pure as to refresh and invigorate the mind while absorbing the thoughts of the gifted author, while the publishers have succeeded in bringing the external into a most felicitous harmony with the inspiration that dwells within. Take it all in all, it is a book we have often dreamed of, but dreamed not that it would ever meet our waking eye as a tangible reality.—*Nashville Journal of Medicine*.

We deem it fortunate that the splendid work of Dr. La Roche should have been issued from the press at this particular time. The want of a reliable digest of all that is known in relation to this frightful malady has long been felt—a want very satisfactorily met in the work before us. We deem it but faint praise to say that Dr. La Roche has succeeded in presenting the profession with an able and complete monograph, one which will find its way into every well ordered library.—*Va. Stethoscope*.

BY THE SAME AUTHOR.

PNEUMONIA; its Supposed Connection, Pathological and Etiological, with Autumnal Fevers, including an Inquiry into the Existence and Morbid Agency of Malaria. In one handsome octavo volume, extra cloth, of 500 pages. \$3 00.

MILLER (HENRY), M. D.,

Professor of Obstetrics and Diseases of Women and Children in the University of Louisville.

PRINCIPLES AND PRACTICE OF OBSTETRICS, &c.; including the Treatment of Chronic Inflammation of the Cervix and Body of the Uterus considered as a frequent cause of Abortion. With about one hundred illustrations on wood. In one very handsome octavo volume, of over 600 pages. (*Now Ready*.) \$3 75.

The reputation of Dr. Miller as an obstetrician is too widely spread to require the attention of the profession to be specially called to a volume containing the experience of his long and extensive practice. The very favorable reception accorded to his "Treatise on Human Parturition," issued some years since, is an earnest that the present work will fulfil the author's intention of providing within a moderate compass a complete and trustworthy text-book for the student, and book of reference for the practitioner. Based to a certain extent upon the former work, but enlarged to more than double its size, and almost wholly rewritten, it presents, besides the matured experience of the author, the most recent views and investigations of modern obstetric writers, such as DUBOIS, CAZEAUX, SIMPSON, TYLER SMITH, &c., thus embodying the results not only of the American, but also of the Paris, the London, and the Edinburgh obstetric schools. The author's position for so many years as a teacher of his favorite branch, has given him a familiarity with the wants of students and a facility of conveying instruction, which cannot fail to render the volume eminently adapted to its purposes.

We congratulate the author that the task is done. We congratulate him that he has given to the medical public a work which will secure for him a high and permanent position among the standard authorities on the principles and practice of obstetrics. Congratulations are not less due to the medical profession of this country, on the acquisition of a treatise embodying the results of the studies, reflections, and experience of Prof. Miller. Few men, if any, in this country, are more competent than he to write on this department of medicine. Engaged for thirty-five years in an extended practice of obstetrics, for many years a teacher of this branch of instruction in one of the largest of our institutions, a diligent student as well as a careful observer, an original and independent thinker, wedded to no hobbies, ever ready to consider without prejudice new views, and to adopt innovations if they are really improvements, and withal a clear, agreeable writer, a practical treatise from his pen could not fail to possess great value. Returning to Prof. Miller's work we have only to add that we hope most sincerely it will be in the hands of every reading and thinking practitioner of this country.—*Buffalo Med Journal*, Mar. 1855.

In fact, this volume must take its place among the standard systematic treatises on obstetrics; a position to which its merits justly entitle it. The style is such that the descriptions are clear, and each subject is discussed and elucidated with due regard to its practical bearings, which cannot fail to make it acceptable and valuable to both students and practitioners. We cannot, however, close this brief notice without congratulating the author and the profession on the production of such an excellent treatise. The author is a western man of whom we feel proud, and we cannot but think that his book will find many readers and warm admirers wherever obstetrics is taught and studied as a science and an art.—*The Cincinnati Lancet and Observer*, Feb. 1855.

A most respectable and valuable addition to our home medical literature, and one reflecting credit alike on the author and the institution to which he is attached. The student will find in this work a most useful guide to his studies; the country practitioner, rusty in his reading, can obtain from its pages a fair resume of the modern literature of the science; and we hope to see this American production generally consulted by the profession.—*Va. Med. Journal*, Feb. 1855.

MEIGS (CHARLES D.), M. D.,
Professor of Obstetrics, &c. in the Jefferson Medical College, Philadelphia.

OBSTETRICS: THE SCIENCE AND THE ART. Third edition, revised and improved. With one hundred and twenty-nine illustrations. In one beautifully printed octavo volume, leather, of seven hundred and fifty-two large pages. \$3 75.

The rapid demand for another edition of this work is a sufficient expression of the favorable verdict of the profession. In thus preparing it a third time for the press, the author has endeavored to render it in every respect worthy of the favor which it has received. To accomplish this he has thoroughly revised it in every part. Some portions have been rewritten, others added, new illustrations have been in many instances substituted for such as were not deemed satisfactory, while, by an alteration in the typographical arrangement, the size of the work has not been increased, and the price remains unaltered. In its present improved form, it is, therefore, hoped that the work will continue to meet the wants of the American profession as a sound, practical, and extended **SYSTEM OF MIDWIFERY.**

Though the work has received only five pages of enlargement, its chapters throughout wear the impress of careful revision. Expunging and rewriting, remodelling its sentences, with occasional new material, all evince a lively desire that it shall deserve to be regarded as improved in *manner* as well as *matter*. In the *matter*, every stroke of the pen has increased the value of the book, both in expungings and additions.—*Western Lancet*, Jan. 1857.

The best American work on Midwifery that is accessible to the student and practitioner.—*N. W. Med. and Surg. Journal*, Jan. 1857.

This is a standard work by a great American Obstetrician. It is the third and last edition, and, in the language of the preface, the author has "brought the subject up to the latest dates of real improvement in our art and Science."—*Nashville Journ. of Med. and Surg.*, May, 1857.

BY THE SAME AUTHOR. (*Lately Issued.*)

WOMAN: HER DISEASES AND THEIR REMEDIES. A Series of Lectures to his Class. Third and Improved edition. In one large and beautifully printed octavo volume, leather. pp. 672. \$3 60.

The gratifying appreciation of his labors, as evinced by the exhaustion of two large impressions of this work within a few years, has not been lost upon the author, who has endeavored in every way to render it worthy of the favor with which it has been received. The opportunity thus afforded for a second revision has been improved, and the work is now presented as in every way superior to its predecessors, additions and alterations having been made whenever the advance of science has rendered them desirable. The typographical execution of the work will also be found to have undergone a similar improvement, and the work is now confidently presented as in every way worthy the position it has acquired as the standard American text-book on the Diseases of Females.

It contains a vast amount of practical knowledge, by one who has accurately observed and retained the experience of many years, and who tells the result in a free, familiar, and pleasant manner.—*Dublin Quarterly Journal*.

There is an off-hand fervor, a glow, and a warm-heartedness infecting the effort of Dr. Meigs, which is entirely captivating, and which absolutely hurries the reader through from beginning to end. Besides, the book teems with solid instruction, and it shows the very highest evidence of ability, viz., the clearness with which the information is presented. We know of no better test of one's understanding a subject than the evidence of the power of lucidly explaining it. The most elementary, as well as the obscurest subjects, under the pencil of Prof. Meigs, are isolated and made to stand out in

such bold relief, as to produce distinct impressions upon the mind and memory of the reader.—*The Charleston Med. Journal*.

Professor Meigs has enlarged and amended this great work, for such it unquestionably is, having passed the ordeal of criticism at home and abroad, but been improved thereby; for in this new edition the author has introduced real improvements, and increased the value and utility of the book immeasurably. It presents so many novel, bright, and sparkling thoughts; such an exuberance of new ideas on almost every page, that we confess ourselves to have become enamored with the book and its author; and cannot withhold our congratulations from our Philadelphia conferees, that such a teacher is in their service.—*N. Y. Med. Gazette*.

BY THE SAME AUTHOR.

ON THE NATURE, SIGNS, AND TREATMENT OF CHILDBED FEVER. In a Series of Letters addressed to the Students of his Class. In one handsome octavo volume, extra cloth, of 365 pages. \$2 50.

The instructive and interesting author of this work, whose previous labors in the department of medicine which he so sedulously cultivates, have placed his countrymen under deep and abiding obligations, again challenges their admiration in the fresh and vigorous, attractive and racy pages before us. It is a delectable book. * * * This treatise upon child-bed fevers will have an extensive sale, being destined, as it deserves, to find a place in the library of every practitioner who scorns to lag in the rear.—*Nashville Journal of Medicine and Surgery*.

This book will add more to his fame than either of those which bear his name. Indeed we doubt whether any material improvement will be made on the teachings of this volume for a century to come, since it is so eminently practical, and based on profound knowledge of the *science* and consummate skill in the *art* of healing, and ratified by an ample and extensive experience, such as few men have the industry or good fortune to acquire.—*N. Y. Med. Gazette*.

BY THE SAME AUTHOR; WITH COLORED PLATES.

A TREATISE ON ACUTE AND CHRONIC DISEASES OF THE NECK OF THE UTERUS. With numerous plates, drawn and colored from nature in the highest style of art. In one handsome octavo volume, extra cloth. \$4 50.

MAYNE'S DISPENSATORY AND THERAPEUTICAL REMEMBRANCER. Comprising the entire lists of *Materia Medica*, with every Practical Formula contained in the three British Pharmacopœias. Edited, with the addition of the Formulas of the U. S. Pharmacopœia, by R. E. GARRICK, M. D. 12mo. vol. ex. cl., 306 pp. 75 c.

MALGAIGNE'S OPERATIVE SURGERY, based on Normal and Pathological Anatomy. Translated from the French by FREDERICK BRITTON, A. B., M. D. With numerous illustrations on wood. In one handsome octavo volume, extra cloth, of nearly six hundred pages. \$3 25.

MACLISE (JOSEPH), SURGEON.**SURGICAL ANATOMY.** Forming one volume, very large imperial quarto.

With sixty-eight large and splendid Plates, drawn in the best style and beautifully colored. Containing one hundred and ninety Figures, many of them the size of life. Together with copious and explanatory letter-press. Strongly and handsomely bound in extra cloth, being one of the cheapest and best executed Surgical works as yet issued in this country. \$11 00.

* * The size of this work prevents its transmission through the post-office as a whole, but those who desire to have copies forwarded by mail, can receive them in five parts, done up in stout wrappers. Price \$9 00.

One of the greatest artistic triumphs of the age in Surgical Anatomy.—*British American Medical Journal*.

Too much cannot be said in its praise; indeed, we have not language to do it justice.—*Ohio Medical and Surgical Journal*.

The most admirable surgical atlas we have seen. To the practitioner deprived of demonstrative dissections upon the human subject, it is an invaluable companion.—*N. J. Medical Reporter*.

The most accurately engraved and beautifully colored plates we have ever seen in an American book—one of the best and cheapest surgical works ever published.—*Buffalo Medical Journal*.

It is very rare that so elegantly printed, so well illustrated, and so useful a work, is offered at so moderate a price.—*Charleston Medical Journal*.

Its plates can boast a superiority which places them almost beyond the reach of competition.—*Medical Examiner*.

Every practitioner, we think, should have a work of this kind within reach.—*Southern Medical and Surgical Journal*.

No such lithographic illustrations of surgical lesions have hitherto, we think, been given.—*Boston Medical and Surgical Journal*.

As a surgical anatomist, Mr. MacLise has probably no superior.—*British and Foreign Medico-Chirurgical Review*.

Of great value to the student engaged in dissecting, and to the surgeon at a distance from the means of keeping up his anatomical knowledge.—*Medical Times*.

A work which has no parallel in point of accuracy and cheapness in the English language.—*N. Y. Journal of Medicine*.

To all engaged in the study or practice of their profession, such a work is almost indispensable.—*Dublin Quarterly Medical Journal*.

Country practitioners will find these plates of immense value.—*N. Y. Medical Gazette*.

We are extremely gratified to announce to the profession the completion of this truly magnificent work, which, as a whole, certainly stands unrivalled, both for accuracy of drawing, beauty of coloring, and all the requisite explanations of the subject in hand.—*The New Orleans Medical and Surgical Journal*.

This is by far the ablest work on Surgical Anatomy that has come under our observation. We know of no other work that would justify a student, in any degree, for neglect of actual dissection. In those sudden emergencies that so often arise, and which require the instantaneous command of minute anatomical knowledge, a work of this kind keeps the details of the dissecting-room perpetually fresh in the memory.—*The Western Journal of Medicine and Surgery*.

☞ The very low price at which this work is furnished, and the beauty of its execution, require an extended sale to compensate the publishers for the heavy expenses incurred.

MORLAND (W. W.), M. D.

Fellow of the Massachusetts Medical Society, &c.

DISEASES OF THE URINARY ORGANS; a Compendium of their Diagnosis, Pathology, and Treatment. With illustrations. In one large and handsome octavo volume, of about 600 pages, extra cloth. (Now ready, Oct. 1853.) Price \$3 50.

This volume, it is hoped, will supply the want of a work presenting within convenient compass the whole subject of the diseases to which all the urinary organs are liable, with their treatment, both medical and surgical. The aim of the author has been throughout to condense the results of the most recent investigations in a clear and succinct manner, omitting nothing of practical importance, without, at the same time, embarrassing the student with unnecessary speculations. Various elaborate and important works have recently appeared on different departments of the subject, but none, it is believed, which thoroughly covers the whole ground in the manner which Dr. Morland has attempted.

MACKENZIE (W.), M. D.,

Surgeon Oculist in Scotland in ordinary to Her Majesty, &c. &c.

A PRACTICAL TREATISE ON DISEASES AND INJURIES OF THE

EYE. To which is prefixed an Anatomical Introduction explanatory of a Horizontal Section of the Human Eyeball, by THOMAS WARTON JONES, F. R. S. From the Fourth Revised and Enlarged London Edition. With Notes and Additions by ADDINELL HEWSON, M. D., Surgeon to Wills Hospital, &c. &c. In one very large and handsome octavo volume, leather, raised bands, with plates and numerous wood-cuts. \$5 25.

The treatise of Dr. Mackenzie indisputably holds the first place, and forms, in respect of learning and research, an Encyclopedia unequalled in extent by any other work of the kind, either English or foreign.—*Dixon on Diseases of the Eye*.

Few modern books on any department of medicine or surgery have met with such extended circulation, or have procured for their authors a like amount of European celebrity. The immense research which it displayed, the thorough acquaintance with the subject, practically as well as theoretically, and the able manner in which the author's stores of learning and experience were rendered available for general use, at once procured for the first edition, as well on the continent as in this country, that high position as a standard work which each successive edition has more firmly established, in spite of the attractions of several rivals of no mean ability. We con-

sider it the duty of every one who has the love of his profession and the welfare of his patient at heart, to make himself familiar with this the most complete work in the English language upon the diseases of the eye.—*Med. Times and Gazette*.

The fourth edition of this standard work will no doubt be as fully appreciated as the three former editions. It is unnecessary to say a word in its praise, for the verdict has already been passed upon it by the most competent judges, and "Mackenzie on the Eye" has justly obtained a reputation which it is no figure of speech to call world-wide.—*British and Foreign Medico-Chirurgical Review*.

This new edition of Dr. Mackenzie's celebrated treatise on diseases of the eye, is truly a miracle of industry and learning. We need scarcely say that he has entirely exhausted the subject of his speciality.—*Dublin Quarterly Journal*.

MILLER (JAMES), F. R. S. E.,

Professor of Surgery in the University of Edinburgh, &c.

PRINCIPLES OF SURGERY. Fourth American, from the third and revised Edinburgh edition. In one large and very beautiful volume, leather, of 700 pages, with two hundred and forty exquisite illustrations on wood. \$3 75.

The work of Mr. Miller is too well and too favorably known among us, as one of our best text-books, to render any further notice of it necessary than the announcement of a new edition, the fourth in our country, a proof of its extensive circulation among us. As a concise and reliable exposition of the science of modern surgery, it stands deservedly high—we know not its superior.—*Boston Med. and Surg. Journal.*

It presents the most satisfactory exposition of the modern doctrines of the principles of surgery to be found in any volume in any language.—*N. Y. Journal of Medicine.*

The work takes rank with Watson's Practice of Physic; it certainly does not fall behind that great work in soundness of principle or depth of reasoning and research. No physician who values his re-

putation, or seeks the interests of his patients, can acquit himself before his God and the world without making himself familiar with the sound and philosophical views developed in the foregoing book.—*New Orleans Med. and Surg. Journal.*

Without doubt the ablest exposition of the principles of that branch of the healing art in any language. This opinion, deliberately formed after a careful study of the first edition, we have had no cause to change on examining the second. This edition has undergone thorough revision by the author; many expressions have been modified, and a mass of new matter introduced. The book is got up in the finest style, and is an evidence of the progress of typography in our country.—*Charleston Medical Journal and Review.*

BY THE SAME AUTHOR. (*Now Ready.*)

THE PRACTICE OF SURGERY. Fourth American from the last Edinburgh edition. Revised by the American editor. Illustrated by three hundred and sixty-four engravings on wood. In one large octavo volume, leather, of nearly 700 pages. \$3 75.

No eulogium of ours could add to the popularity of Miller's Surgery. Its reputation in this country is unsurpassed by that of any other work, and, when taken in connection with the author's *Principles of Surgery*, constitutes a whole, without reference to to which no conscientious surgeon would be willing practice his art.—*Southern Med. and Surg. Journal.*

It is seldom that two volumes have ever made so profound an impression in so short a time as the "Principles" and the "Practice" of Surgery by Mr. Miller—or so richly merited the reputation they have acquired. The author is an eminently sensible, practical, and well-informed man, who knows exactly what he is talking about and exactly how to talk it.—*Kentucky Medical Recorder.*

By the almost unanimous voice of the profession,

his works, both on the principles and practice of surgery have been assigned the highest rank. If we were limited to but one work on surgery, that one should be Miller's, as we regard it as superior to all others.—*St. Louis Med. and Surg. Journal.*

The author has in this and his "Principles," presented to the profession one of the most complete and reliable systems of Surgery extant. His style of writing is original, impressive, and engaging, energetic, concise, and lucid. Few have the faculty of condensing so much in small space, and at the same time so persistently holding the attention. Whether as a text-book for students or a book of reference for practitioners, it cannot be too strongly recommended.—*Southern Journal of Med. and Physical Sciences.*

MONTGOMERY (W. F.), M. D., M. R. I. A., &c.,

Professor of Midwifery in the King and Queen's College of Physicians in Ireland, &c.

AN EXPOSITION OF THE SIGNS AND SYMPTOMS OF PREGNANCY.

With some other Papers on Subjects connected with Midwifery. From the second and enlarged English edition. With two exquisite colored plates, and numerous wood-cuts. In one very handsome octavo volume, extra cloth, of nearly 600 pages. (*Just Issued, 1857.*) \$3 75.

The present edition of this classical volume is fairly entitled to be regarded as a new work, every sentence having been carefully rewritten, and the whole increased to more than double the original size. The title of the work scarcely does justice to the extent and importance of the topics brought under consideration, embracing, with the exception of the operative procedures of midwifery, almost everything connected with obstetrics, either directly or incidentally; and there are few physicians who will not find in its pages much that will prove of great interest and value in their daily practice. The special Essays on the Period of Human Gestation, the Signs of Delivery, and the Spontaneous Amputation and other Lesions of the Fœtus in Utero present topics of the highest interest fully treated and beautifully illustrated.

In every point of mechanical execution the work will be found one of the handsomest yet issued from the American press.

A book unusually rich in practical suggestions.—*Am. Journal Med. Sciences, Jan. 1857.*

Those several subjects so interesting in themselves, and so important, every one of them, to the most delicate and precious of social relations, controlling often the honor and domestic peace of a family, the legitimacy of offspring, or the life of its parent, are all treated with an elegance of diction, fulness of illustrations, acuteness and justice of reasoning, unparalleled in obstetrics, and unsurpassed in medicine. The reader's interest can never flag, so fresh, and vigorous, and classical is our author's style; and one forgets, in the renewed charm of every page, that it, and every line, and every word

has been weighed and reweighed through years of preparation; that this is of all others the book of Obstetric Law, on each of its several topics; on all points connected with pregnancy, to be everywhere received as a manual of special jurisprudence, at once announcing fact, affording argument, establishing precedent, and governing alike the jurymen, advocate, and judge. It is not merely in its legal relations that we find this work so interesting. Hardly a page but that has its hints or facts important to the general practitioner; and not a chapter without especial matter for the anatomist, physiologist, or pathologist.—*N. A. Med.-Chir. Review, March, 1857.*

MOHR (FRANCIS), PH. D., AND REDWOOD (THEOPHILUS).

PRACTICAL PHARMACY. Comprising the Arrangements, Apparatus, and Manipulations of the Pharmaceutical Shop and Laboratory. Edited, with extensive Additions, by Prof. WILLIAM PROCTER, of the Philadelphia College of Pharmacy. In one handsomely printed octavo volume, extra cloth, of 570 pages, with over 500 engravings on wood. \$2 75.

NEILL (JOHN), M. D.,

Surgeon to the Pennsylvania Hospital, &c.; and

FRANCIS GURNEY SMITH, M. D.,

Professor of Institutes of Medicine in the Pennsylvania Medical College.

AN ANALYTICAL COMPENDIUM OF THE VARIOUS BRANCHES

OF MEDICAL SCIENCE; for the Use and Examination of Students. A new edition, revised and improved. In one very large and handsomely printed royal 12mo. volume, of about one thousand pages, with 374 wood-cuts. Strongly bound in leather, with raised bands. \$3 00.

The very flattering reception which has been accorded to this work, and the high estimate placed upon it by the profession, as evinced by the constant and increasing demand which has rapidly exhausted two large editions, have stimulated the authors to render the volume in its present revision more worthy of the success which has attended it. It has accordingly been thoroughly examined, and such errors as had on former occasions escaped observation have been corrected, and whatever additions were necessary to maintain it on a level with the advance of science have been introduced. The extended series of illustrations has been still further increased and much improved, while, by a slight enlargement of the page, these various additions have been incorporated without increasing the bulk of the volume.

The work is, therefore, again presented as eminently worthy of the favor with which it has hitherto been received. As a book for daily reference by the student requiring a guide to his more elaborate text-books, as a manual for preceptors desiring to stimulate their students by frequent and accurate examination, or as a source from which the practitioners of older date may easily and cheaply acquire a knowledge of the changes and improvement in professional science, its reputation is permanently established.

The best work of the kind with which we are acquainted.—*Med. Examiner.*

Having made free use of this volume in our examinations of pupils, we can speak from experience in recommending it as an admirable compend for students, and as especially useful to preceptors who examine their pupils. It will save the teacher much labor by enabling him readily to recall all of the points upon which his pupils should be examined. A work of this sort should be in the hands of every one who takes pupils into his office with a view of examining them; and this is unquestionably the best of its class.—*Transylvania Med. Journal.*

In the rapid course of lectures, where work for

the students is heavy, and review necessary for an examination, a compend is not only valuable, but it is almost a *sine qua non*. The one before us is, in most of the divisions, the most unexceptionable of all books of the kind that we know of. The newest and soundest doctrines and the latest improvements and discoveries are explicitly, though concisely, laid before the student. There is a class to whom we very sincerely commend this cheap book as worth its weight in silver—that class is the graduates in medicine of more than ten years' standing, who have not studied medicine since. They will perhaps find out from it that the science is not exactly now what it was when they left it off.—*The Spectator*

NEILL (JOHN), M. D.,

Professor of Surgery in the Pennsylvania Medical College, &c.

OUTLINES OF THE VEINS AND LYMPHATICS. With handsome colored plates. 1 vol., cloth. \$1 25.

OUTLINES OF THE NERVES. With handsome plates. 1 vol., cloth. \$1 25.

NELIGAN (J. MOORE), M. D., M. R. I. A., &c.

(A splendid work. Just Issued.)

ATLAS OF CUTANEOUS DISEASES. In one beautiful quarto volume, extra cloth, with splendid colored plates, presenting nearly one hundred elaborate representations of disease. \$4 50.

This beautiful volume is intended as a complete and accurate representation of all the varieties of Diseases of the Skin. While it can be consulted in conjunction with any work on Practice, it has especial reference to the author's "Treatise on Diseases of the Skin," so favorably received by the profession some years since. The publishers feel justified in saying that few more beautifully executed plates have ever been presented to the profession of this country.

A compend which will very much aid the practitioner in this difficult branch of diagnosis. Taken with the beautiful plates of the Atlas, which are remarkable for their accuracy and beauty of coloring, it constitutes a very valuable addition to the library of a practical man.—*Buffalo Med. Journal*, Sept. 1856.

Nothing is often more difficult than the diagnosis of disease of the skin; and hitherto, the only works containing illustrations have been at rather inconvenient prices—prices, indeed, that prevented general use. The work before us will supply a want long felt, and minister to a more perfect acquaintance with the nature and treatment of a very frequent and troublesome form of disease.—*Ohio Med. and Surg. Journal*, July, 1856.

Neligan's Atlas of Cutaneous Diseases supplies a

long existent desideratum much felt by the largest class of our profession. It presents, in quarto size, 16 plates, each containing from 3 to 6 figures, and forming in all a total of 90 distinct representations of the different species of skin affections, grouped together in genera or families. The illustrations have been taken from nature, and have been copied with such fidelity that they present a striking picture of life; in which the reduced scale aptly serves to give, at a coup d'œil, the remarkable peculiarities of each individual variety. And while thus the disease is rendered more definable, there is yet no loss of proportion incurred by the necessary concentration. Each figure is highly colored, and so truthful has the artist been that the most fastidious observer could not justly take exception to the correctness of the execution of the pictures under his scrutiny.—*Montreal Med. Chronicle.*

BY THE SAME AUTHOR.

A PRACTICAL TREATISE ON DISEASES OF THE SKIN. Second American edition. In one neat royal 12mo. volume, extra cloth, of 334 pages. \$1 00.

The two volumes will be sent by mail on receipt of *Five Dollars*.

OWEN ON THE DIFFERENT FORMS OF THE SKELETON, AND OF THE TEETH.

One vol. royal 12mo., extra cloth, with numerous illustrations. \$1 25.

PEASLEE (E. R.), M. D.,

Professor of Physiology and General Pathology in the New York Medical College.

HUMAN HISTOLOGY, in its relations to Anatomy, Physiology, and Pathology; for the use of Medical Students. With four hundred and thirty-four illustrations. In one handsome octavo volume, of over 600 pages. (*Now Ready, 1858.*) \$3 75.

It embraces a library upon the topics discussed within itself, and is just what the teacher and learner need. Another advantage, by no means to be overlooked, everything of real value in the wide range which it embraces, is with great skill compressed into an octavo volume of but little more than six hundred pages. We have not only the whole subject of Histology, interesting in itself, ably and fully discussed, but what is of infinitely greater interest to the student, because of greater practical value, are its relations to Anatomy, Physiology, and Pathology, which are here fully and satisfactorily set forth. These great supporting branches of practical medicine are thus linked together, and while establishing and illustrating each other, are interwoven into a harmonious whole. We commend the work to students and physicians generally.—*Nashville Journ. of Med. and Surgery*, Dec. 1857.

It far surpasses our expectation. We never conceived the possibility of compressing so much valuable information into so compact a form. We will not consume space with commendations. We re-

ceive this contribution to physiological science, "Not with vain thanks, but with acceptance boateous." We have already paid it the practical compliment of making abundant use of it in the preparation of our lectures, and also of recommending its further perusal most cordially to our alumni; a recommendation which we now extend to our readers.—*Memphis Med. Recorder*, Jan. 1858.

We would recommend it to the medical student and practitioner, as containing a summary of all that is known of the important subjects which it treats; of all that is contained in the great works of Simon and Lehmann, and the organic chemists in general. Master this one volume, we would say to the medical student and practitioner—master this book and you know all that is known of the great fundamental principles of medicine, and we have no hesitation in saying that it is an honor to the American medical profession that one of its members should have produced it.—*St. Louis Med. and Surg. Journal*, March, 1858.

PEREIRA (JONATHAN), M. D., F. R. S., AND L. S.

THE ELEMENTS OF MATERIA MEDICA AND THERAPEUTICS.

Third American edition, enlarged and improved by the author; including Notices of most of the Medicinal Substances in use in the civilized world, and forming an Encyclopedia of Materia Medica. Edited, with Additions, by JOSEPH CARSON, M. D., Professor of Materia Medica and Pharmacy in the University of Pennsylvania. In two very large octavo volumes of 2100 pages, on small type, with about 500 illustrations on stone and wood, strongly bound in leather, with raised bands. \$9 00.

PARRISH (EDWARD),

Lecturer on Practical Pharmacy and Materia Medica in the Pennsylvania Academy of Medicine, &c.

AN INTRODUCTION TO PRACTICAL PHARMACY. Designed as a Text-Book for the Student, and as a Guide for the Physician and Pharmacist. With many Formulæ and Prescriptions. In one handsome octavo volume, extra cloth, of 550 pages, with 243 Illustrations. \$2 75.

A careful examination of this work enables us to speak of it in the highest terms, as being the best treatise on practical pharmacy with which we are acquainted, and an invaluable *padre-mecum*, not only to the apothecary and to those practitioners who are accustomed to prepare their own medicines, but to every medical man and medical student. Throughout the work are interspersed valuable tables, useful formulæ, and practical hints, and the whole is illustrated by a large number of excellent wood-engravings.—*Boston Med. and Surg. Journal*.

This is altogether one of the most useful books we have seen. It is just what we have long felt to be needed by apothecaries, students, and practitioners of medicine, most of whom in this country have to put up their own prescriptions. It bears, upon every page, the impress of practical knowledge, conveyed in a plain common sense manner, and adapted to the comprehension of all who may read it. No detail has been omitted, however trivial it may seem, although really important to the dispenser of medicine.—*Southern Med. and Surg. Journal*.

To both the country practitioner and the city apothecary this work of Mr. Parrish is a godsend. A careful study of its contents will give the young graduate a familiarity with the value and mode of administering his prescriptions, which will be of as much use to his patient as to himself.—*Va. Med. Journal*.

Mr. Parrish has rendered a very acceptable service to the practitioner and student, by furnishing this

book, which contains the leading facts and principles of the science of Pharmacy, conveniently arranged for study, and with special reference to those features of the subject which possess an especial practical interest to the physician. It furnishes the student, at the commencement of his studies, with that information which is of the greatest importance in initiating him into the domain of Chemistry and Materia Medica; it familiarizes him with the compounding of drugs, and supplies those minutiae which but few practitioners can impart. The junior practitioner will, also, find this volume replete with instruction.—*Charleston Med. Journal and Review*, Mar. 1856.

There is no useful information in the details of the apothecary's or country physician's office conducted according to science that is omitted. The young physician will find it an encyclopedia of indispensable medical knowledge, from the purchase of a spatula to the compounding of the most learned prescriptions. The work is by the ablest pharmacist in the United States, and must meet with an immense sale.—*Nashville Journal of Medicine*, April, 1856.

We are glad to receive this excellent work. It will supply a want long felt by the profession, and especially by the student of Pharmacy. A large majority of physicians are obliged to compound their own medicines, and to them a work of this kind is indispensable.—*N. O. Medical and Surgical Journal*.

PARKER (LANGSTON),

Surgeon to the Queen's Hospital, Birmingham.

THE MODERN TREATMENT OF SYPHILITIC DISEASES, BOTH PRIMARY AND SECONDARY; comprising the Treatment of Constitutional and Confirmed Syphilis, by a safe and successful method. With numerous Cases, Formulæ, and Clinical Observations. From the Third and entirely rewritten London edition. In one neat octavo volume, extra cloth, of 316 pages. \$1 75.

PIRRIE (WILLIAM), F. R. S. E.,

Professor of Surgery in the University of Aberdeen.

THE PRINCIPLES AND PRACTICE OF SURGERY. Edited by JOHN

NEILL, M. D., Professor of Surgery in the Penna. Medical College, Surgeon to the Pennsylvania Hospital, &c. In one very handsome octavo volume, leather, of 780 pages, with 316 illustrations. \$3 75.

We know of no other surgical work of a reasonable size, wherein there is so much theory and practice, or where subjects are more soundly or clearly taught.—*The Stethoscope*.

There is scarcely a disease of the bones or soft parts, fracture, or dislocation, that is not illustrated by accurate wood-engravings. Then, again, every instrument employed by the surgeon is thus represented. These engravings are not only correct, but

really beautiful, showing the astonishing degree of perfection to which the art of wood-engraving has arrived. Prof. Pirrie, in the work before us, has elaborately discussed the principles of surgery, and a safe and effectual practice predicated upon them. Perhaps no work upon this subject heretofore issued is so full upon the science of the art of surgery.—*Nashville Journal of Medicine and Surgery*.

RICORD (P.), M. D.,

A TREATISE ON THE VENEREAL DISEASE. By JOHN HUNTER, F. R. S.

With copious Additions, by P. RICORD, M. D. Translated and Edited, with Notes, by FREEMAN J. BUMSTEAD, M. D., Lecturer on Venereal at the College of Physicians and Surgeons, New York. Second edition, revised, containing a *résumé* of RICORD'S RECENT LECTURES ON CHANCER. In one handsome octavo volume, extra cloth, of 550 pages, with eight plates. \$3 25. (*Now Ready*, December, 1856.)

In revising this work, the editor has endeavored to introduce whatever matter of interest the recent investigations of syphilographers have added to our knowledge of the subject. The principal source from which this has been derived is the volume of "Lectures on Chancere," published a few months since by M. Ricord, which affords a large amount of new and instructive material on many controverted points. In the previous edition, M. Ricord's additions amounted to nearly one-third of the whole, and with the matter now introduced, the work may be considered to present his views and experience more thoroughly and completely than any other. The value of the original treatise of Mr. Hunter is too well known to require praise. Perhaps no medical work in the English language has so thoroughly stood the test of time, or has so completely assumed the position of a classic, and a volume like the present, containing the united labors of the highest authorities on so difficult and important a subject, becomes indispensable to all who desire to keep themselves on a level with the progress of medical science.

Every one will recognize the attractiveness and value which this work derives from thus presenting the opinions of these two masters side by side. But it must be admitted, what has made the fortune of the book, is the fact that it contains the "most complete embodiment of the veritable doctrines of the Hôpital du Midi," which has ever been made public. The doctrinal ideas of M. Ricord, ideas which, if not universally adopted, are incontestably dominant, have heretofore only been interpreted by more or less skilful

secretaries, sometimes accredited and sometimes not.

In the notes to Hunter, the master substitutes himself for his interpreters, and gives his original thoughts to the world in a lucid and perfectly intelligible manner. In conclusion we can say that this is incontestably the best treatise on syphilis with which we are acquainted, and, as we do not often employ the phrase, we may be excused for expressing the hope that it may find a place in the library of every physician.—*Virginia Med. and Surg. Journal*.

BY THE SAME AUTHOR.

RICORD'S LETTERS ON SYPHILIS. Translated by W. P. LATTIMORE, M. D.

In one neat octavo volume, of 270 pages, extra cloth. \$2 00.

ROKITANSKY (CARL), M. D.,

Curator of the Imperial Pathological Museum, and Professor at the University of Vienna, &c.

A MANUAL OF PATHOLOGICAL ANATOMY. Four volumes, octavo,

bound in two, extra cloth, of about 1200 pages. Translated by W. E. SWAINE, EDWARD SIEVEKING, C. H. MOORE, and G. E. DAY. \$5 50

The profession is too well acquainted with the reputation of Rokitansky's work to need our assurance that this is one of the most profound, thorough, and valuable books ever issued from the medical press. It is *sui generis*, and has no standard of comparison. It is only necessary to announce that it is issued in a form as cheap as is compatible with its size and preservation, and its sale follows as a matter of course. No library can be called complete without it.—*Buffalo Med. Journal*.

An attempt to give our readers any adequate idea of the vast amount of instruction accumulated in these volumes, would be feeble and hopeless. The effort of the distinguished author to concentrate in a small space his great fund of knowledge, has

so charged his text with valuable truths, that any attempt of a reviewer to epitomize is at once paralyzed, and must end in a failure.—*Western Lancet*.

As this is the highest source of knowledge upon the important subject of which it treats, no real student can afford to be without it. The American publishers have entitled themselves to the thanks of the profession of their country, for this timely and beautiful edition.—*Nashville Journal of Medicine*.

As a book of reference, therefore, this work must prove of inestimable value, and we cannot too highly recommend it to the profession.—*Charleston Med. Journal and Review*.

This book is a necessity to every practitioner.—*Am. Med. Monthly*.

RIGBY (EDWARD), M. D.,

Senior Physician to the General Lying-in Hospital, &c.

A SYSTEM OF MIDWIFERY. With Notes and Additional Illustrations.

Second American Edition. One volume octavo, extra cloth, 422 pages. \$2 50.

BY THE SAME AUTHOR. (*Now Ready*, 1857.)

ON THE CONSTITUTIONAL TREATMENT OF FEMALE DISEASES.

In one neat royal 12mo. volume, extra cloth, of about 250 pages. \$1 00.

ROYLE'S MATERIA MEDICA AND THERAPEUTICS; including the

Preparations of the Pharmacopœias of London, Edinburgh, Dublin, and of the United States. With many new medicines. Edited by JOSEPH CARSON, M. D. With ninety-eight illustrations. In one large octavo volume, extra cloth, of about 700 pages. \$3 00.

RAMSBOTHAM (FRANCIS H.), M. D.

THE PRINCIPLES AND PRACTICE OF OBSTETRIC MEDICINE AND SURGERY, in reference to the Process of Parturition. A new and enlarged edition, thoroughly revised by the Author. With Additions by W. V. KEATING, M. D. In one large and handsome imperial octavo volume, of 650 pages, strongly bound in leather, with raised bands; with sixty-four beautiful Plates, and numerous Wood-cuts in the text, containing in all nearly two hundred large and beautiful figures. \$5 00.

In calling the attention of the profession to the new edition of this standard work, the publishers would remark that no efforts have been spared to secure for it a continuance and extension of the remarkable favor with which it has been received. The last London issue, which was considerably enlarged, has received a further revision from the author, especially for this country. Its passage through the press here has been supervised by Dr. Keating, who has made numerous additions with a view of presenting more fully whatever was necessary to adapt it thoroughly to American modes of practice. In its mechanical execution, a like superiority over former editions will be found.

From Prof. Hodge, of the University of Pa.

To the American public, it is most valuable, from its intrinsic undoubted excellence, and as being the best authorized exponent of British Midwifery. Its circulation will, I trust, be extensive throughout our country.

The publishers have shown their appreciation of the merits of this work and secured its success by the truly elegant style in which they have brought it out, excelling themselves in its production, especially in its plates. It is dedicated to Prof. Meigs, and has the emphatic endorsement of Prof. Hodge, as the best exponent of British Midwifery. We know of no text-book which deserves in all respects to be more highly recommended to students, and we could wish to see it in the hands of every practitioner, for they will find it invaluable for reference.—*Med. Gazette.*

But once in a long time some brilliant genius rears his head above the horizon of science, and illuminates and purifies every department that he investigates; and his works become types, by which innumerable imitators model their feeble productions. Such a genius we find in the younger Ramsbotham, and such a type we find in the work now before us. The binding, paper, type, the engravings and woodcuts are all so excellent as to make this book one of the finest specimens of the art of printing that have given such a world-wide reputation to its enterprising and liberal publishers. We welcome Ramsbotham's Principles and Practice of Obstetric Medi-

cine and Surgery to our library, and confidently recommend it to our readers, with the assurance that it will not disappoint their most sanguine expectations.—*Western Lancet.*

It is unnecessary to say anything in regard to the utility of this work. It is already appreciated in our country for the value of the matter, the clearness of its style, and the fineness of its illustrations. To the physician's library it is indispensable, while to the student as a text-book, from which to extract the material for laying the foundation of an education on obstetrical science, it has no superior.—*Ohio Med. and Surg. Journal.*

We will only add that the student will learn from it all he need to know, and the practitioner will find it, as a book of reference, surpassed by none other.—*Stethoscope.*

The character and merits of Dr. Ramsbotham's work are so well known and thoroughly established, that comment is unnecessary and praise superfluous. The illustrations, which are numerous and accurate, are executed in the highest style of art. We cannot too highly recommend the work to our readers.—*St. Louis Med. and Surg. Journal.*

SCHOEDLER (FRIEDRICH), PH. D.,

Professor of the Natural Sciences at Worms, &c.

THE BOOK OF NATURE; an Elementary Introduction to the Sciences of Physics, Astronomy, Chemistry, Mineralogy, Geology, Botany, Zoology, and Physiology. First American edition, with a Glossary and other Additions and Improvements; from the second English edition. Translated from the sixth German edition, by HENRY MEDLOCK, F. C. S., &c. In one volume, small octavo, extra cloth, pp. 692, with 679 illustrations. \$1 80.

SMITH (HENRY H.), M. D.,

Professor of Surgery in the University of Pennsylvania, &c.

MINOR SURGERY; or, Hints on the Every-day Duties of the Surgeon. Illustrated by two hundred and forty-seven illustrations. Third and enlarged edition. In one handsome royal 12mo. volume. pp. 456. In leather, \$2 25; extra cloth, \$2 00.

BY THE SAME AUTHOR, AND

HORNER (WILLIAM E.), M. D.,

Late Professor of Anatomy in the University of Pennsylvania.

AN ANATOMICAL ATLAS, illustrative of the Structure of the Human Body.

In one volume, large imperial octavo, extra cloth, with about six hundred and fifty beautiful figures. \$3 00.

These figures are well selected, and present a complete and accurate representation of that wonderful fabric, the human body. The plan of this Atlas, which renders it so peculiarly convenient to the student, and its superb artistic execution, have been already pointed out. We must congratulate

the student upon the completion of this Atlas, as it is the most convenient work of the kind that has yet appeared; and we must add, the very beautiful manner in which it is "got up" is so creditable to the country as to be flattering to our national pride.—*American Medical Journal.*

SMITH (W. TYLER), M. D.,

Physician Accoucheur to St. Mary's Hospital, &c.

ON PARTURITION, AND THE PRINCIPLES AND PRACTICE OF OBSTETRICS. In one royal 12mo. volume, extra cloth, of 400 pages. \$1 25.

BY THE SAME AUTHOR.

A PRACTICAL TREATISE ON THE PATHOLOGY AND TREATMENT OF LEUCORRHEA. With numerous illustrations. In one very handsome octavo volume, extra cloth, of about 250 pages. \$1 50.

SHARPEY (WILLIAM), M. D., JONES QUAIN, M. D., AND
RICHARD QUAIN, F. R. S., &c.

HUMAN ANATOMY. Revised, with Notes and Additions, by JOSEPH LEIDY, M. D., Professor of Anatomy in the University of Pennsylvania. Complete in two large octavo volumes, leather, of about thirteen hundred pages. Beautifully illustrated with over five hundred engravings on wood. \$6 00.

We have no hesitation in recommending this treatise on anatomy as the most complete on that subject in the English language; and the only one, perhaps, in any language, which brings the state of knowledge forward to the most recent discoveries.—*The Edinburgh Med. and Surg. Journal.*

SARGENT (F. W.), M. D.

ON BANDAGING AND OTHER OPERATIONS OF MINOR SURGERY.

Second edition, enlarged. One handsome royal 12mo. vol., of nearly 400 pages, with 182 woodcuts. Extra cloth, \$1 40; leather, \$1 50.

Sargent's Minor Surgery has always been popular, and deservedly so. It furnishes that knowledge of the most frequently requisite performances of surgical art which cannot be entirely understood by attending clinical lectures. The art of bandaging, which is regularly taught in Europe, is very frequently overlooked by teachers in this country; the student and junior practitioner, therefore, may often require that knowledge which this little volume so tersely and happily supplies.—*Charleston Med. Journ. and Review*, March, 1856.

A work that has been so long and favorably known to the profession as Dr. Sargent's Minor Surgery, needs no commendation from us. We would remark, however, in this connection, that minor surgery seldom gets that attention in our schools that its importance deserves. Our larger works are also very defective in their teaching on these small practical points. This little book will supply the void which all must feel who have not studied its pages.—*Western Lancet*, March, 1856.

SKEY'S OPERATIVE SURGERY. In one very handsome octavo volume, extra cloth, of over 650 pages, with about one hundred woodcuts. \$3 25.

STANLEY'S TREATISE ON DISEASES OF THE BONES. In one volume, octavo, extra cloth, 256 pages. \$1 50.

SOULLY ON THE HUMAN BRAIN; its Structure, Physiology, and Diseases. From the Second and

much enlarged London edition. In one octavo volume, extra cloth, of 500 pages, with 120 woodcuts. \$2 00.

SIMON'S GENERAL PATHOLOGY, as conducive to the Establishment of Rational Principles for the prevention and Cure of Disease. In one neat octavo volume, extra cloth, of 212 pages. \$1 25.

TANNER (T. H.), M. D.,
Physician to the Hospital for Women, &c.

A MANUAL OF CLINICAL MEDICINE AND PHYSICAL DIAGNOSIS.

To which is added The Code of Ethics of the American Medical Association. Second American Edition. In one neat volume, small 12mo., extra cloth, 87½ cents.

The work is an honor to its writer, and must obtain a wide circulation by its intrinsic merit alone. Sifted alike to the wants of students and practi-

tioners, it has only to be seen, to win for itself a place upon the shelves of every medical library.—*Boston Med. and Surg. Journal.*

Now Complete.

TODD (ROBERT BENTLEY), M. D., F. R. S.,

Professor of Physiology in King's College, London; and

WILLIAM BOWMAN, F. R. S.,

Demonstrator of Anatomy in King's College, London.

THE PHYSIOLOGICAL ANATOMY AND PHYSIOLOGY OF MAN. With

about three hundred large and beautiful illustrations on wood. Complete in one large octavo volume, of 950 pages, leather. Price \$4 50.

☞ Gentlemen who have received portions of this work, as published in the "MEDICAL NEWS AND LIBRARY," can now complete their copies, if immediate application be made. It will be furnished as follows, free by mail, in paper covers, with cloth backs.

PARTS I., II., III. (pp. 25 to 552), \$2 50.

PART IV. (pp. 553 to end, with Title, Preface, Contents, &c.), \$2 00.

Or, PART IV., SECTION II. (pp. 725 to end, with Title, Preface, Contents, &c.), \$1 25.

A magnificent contribution to British medicine, and the American physician who shall fail to peruse it, will have failed to read one of the most instructive books of the nineteenth century.—*N. O. Med. and Surg. Journal*, Sept. 1857.

It is more concise than Carpenter's Principles, and more modern than the accessible edition of Møller's Elements; its details are brief, but sufficient; its descriptions vivid; its illustrations exact and copious; and its language terse and perspicuous.—*Charleston Med. Journal*, July, 1857.

We know of no work on the subject of physiology so well adapted to the wants of the medical student. Its completion has been thus long delayed, that the authors might secure accuracy by personal observation.—*St. Louis Med. and Surg. Journal*, Sept. '57.

One of the very best books ever issued from any medical press. We think it indispensable to every reading medical man, and it may, with all propriety, and with the utmost advantage be made a text-book by any student who would thoroughly comprehend the groundwork of medicine.—*N. O. Med. News*, June, 1857.

Our notice, though it conveys but a very feeble and imperfect idea of the magnitude and importance of the work now under consideration, already transcends our limits; and, with the indulgence of our readers, and the hope that they will peruse the book for themselves, as we feel we can with confidence recommend it, we leave it in their hands for them to judge of its merits.—*The Northwestern Med. and Surg. Journal*, Oct. 1857.

TODD (R. B.), M. D., F. R. S., &c.

CLINICAL LECTURES ON CERTAIN DISEASES OF THE URINARY ORGANS AND ON DROPSIES. In one octavo volume. (Just Issued, 1857.) \$1 50.

TAYLOR (ALFRED S.), M. D., F. R. S.,
Lecturer on Medical Jurisprudence and Chemistry in Gay's Hospital.

MEDICAL JURISPRUDENCE. Fourth American Edition. With Notes and References to American Decisions, by EDWARD HARTSHORN, M. D. In one large octavo volume, leather, of over seven hundred pages. \$3 00.

This standard work has lately received a very thorough revision at the hands of the author, who has introduced whatever was necessary to render it complete and satisfactory in carrying out the objects in view. The editor has likewise used every exertion to make it equally thorough with regard to all matters relating to the practice of this country. In doing this, he has carefully examined all that has appeared on the subject since the publication of the last edition, and has incorporated all the new information thus presented. The work has thus been considerably increased in size, notwithstanding which, it has been kept at its former very moderate price, and in every respect it will be found worthy of a continuance of the remarkable favor which has carried it through so many editions on both sides of the Atlantic. A few notices of the former editions are appended.

We know of no work on Medical Jurisprudence which contains in the same space anything like the same amount of valuable matter.—*N. Y. Journal of Medicine.*

No work upon the subject can be put into the hands of students either of law or medicine which will engage them more closely or profitably; and none could be offered to the busy practitioner of either calling, for the purpose of casual or hasty reference, that would be more likely to afford the aid desired. We therefore recommend it as the best and safest manual for daily use.—*American Journal of Medical Sciences.*

This work of Dr. Taylor's is generally acknowledged to be one of the ablest extant on the subject of medical jurisprudence. It is certainly one of the most attractive books that we have met with; supplying so much both to interest and instruct, that

we do not hesitate to affirm that after having once commenced its perusal, few could be prevailed upon to desist before completing it. In the last London edition, all the newly observed and accurately recorded facts have been inserted, including much that is recent of Chemical, Microscopical, and Pathological research, besides papers on numerous subjects never before published.—*Charleston Medical Journal and Review.*

It is not excess of praise to say that the volume before us is the very best treatise extant on Medical Jurisprudence. In saying this, we do not wish to be understood as detracting from the merits of the excellent works of Beck, Ryan, Traill, Guy, and others; but in interest and value we think it must be conceded that Taylor is superior to anything that has preceded it.—*N. W. Medical and Surg. Journal.*

BY THE SAME AUTHOR. (*Nearly Ready.*)

ON POISONS, IN RELATION TO MEDICAL JURISPRUDENCE AND MEDICINE. Second American, from a second and revised London edition. In one large octavo volume.

The length of time which has elapsed since the first appearance of this work, has wrought so great a change in the subject, as to require a very thorough revision to adapt the volume to the present wants of the profession. The rapid advance of Chemistry has introduced into use many new substances which may become fatal through accident, carelessness, or design—while at the same time it has likewise designated new and more exact modes of counteracting or detecting those previously treated of. Mr. Taylor's position as the leading medical jurist of England, has during this period conferred on him extraordinary advantages in acquiring experience in all that relates to this department, nearly all cases of moment being referred to him for examination, as an expert whose testimony is generally accepted as final. The results of his labors, therefore, as gathered together in this volume, carefully weighed and sifted, and presented in the clear and intelligible style for which he is noted, may be received as an acknowledged authority, and as a guide to be followed with implicit confidence.

WILSON (MARRIS), M. D.

ON DISEASES OF THE VESICULÆ SEMINALES. See "LALLEMAND," page 19.

WILLIAMS (C. J. B.), M. D., F. R. S.,
Professor of Clinical Medicine in University College, London, &c.

PRINCIPLES OF MEDICINE. An Elementary View of the Causes, Nature, Treatment, Diagnosis, and Prognosis of Disease; with brief remarks on Hygienics, or the preservation of health. A new American, from the third and revised London edition. In one octavo volume, leather, of about 500 pages. \$2 50. (*Just Issued.*)

The very recent and thorough revision which this work has enjoyed at the hands of the author has brought it so completely up to the present state of the subject that in reproducing it no additions have been found necessary. The success which the work has heretofore met shows that its importance has been appreciated, and in its present form it will be found eminently worthy a continuance of the same favor, possessing as it does the strongest claims to the attention of the medical student and practitioner, from the admirable manner in which the various inquiries in the different branches of pathology are investigated, combined and generalised by an experienced practical physician, and directly applied to the investigation and treatment of disease.

We find that the deeply-interesting matter and style of this book have so far fascinated us, that we have unconsciously hung upon its pages, not too long, indeed, for our own profit, but longer than reviewers can be permitted to indulge. We leave the further analysis to the student and practitioner. Our judgment of the work has already been sufficiently expressed. It is a judgment of almost unqualified praise. The work is not of a controversial, but of a didactic character; and as such we hail it, and

recommend it for a text-book, guide, and constant companion to every practitioner and every student who wishes to extricate himself from the well-worn ruts of empiricism, and to base his practice of medicine upon principles.—*London Lancet.*

A text-book to which no other in our language is comparable.—*Charleston Medical Journal.*

No work has ever achieved or maintained a more deserved reputation.—*Va. Med. and Surg. Journal.*

WHITEHEAD ON THE CAUSES AND TREATMENT OF ABORTION AND STERILITY.

Second American Edition. In one volume, octavo, extra cloth, pp. 308. \$1 75.

New and much enlarged edition—(Now Ready, Oct. 1858.)

WATSON (THOMAS), M. D., &c.

Late Physician to the Middlesex Hospital, &c.

LECTURES ON THE PRINCIPLES AND PRACTICE OF PHYSIC.

Delivered at King's College, London. A new American, from the last revised and enlarged English edition, with Additions, by D. FRANCIS CONNIE, M. D., author of "A Practical Treatise on the Diseases of Children," &c. With one hundred and eighty-five illustrations on wood. In one very large and handsome volume, imperial octavo, of over 1200 closely printed pages in small type; the whole strongly bound in leather, with raised bands. Price \$4 25.

The publishers feel that they are rendering a service to the American profession in presenting at so very moderate a price this vast body of sound practical information. Whether as a guide for the student entering on a course of instruction, or as a book of reference for daily consultation by the practitioner, "Watson's Practice" has long been regarded as second to none; the soundness and fulness of its teachings, the breadth and liberality of its views, and the easy and flowing style in which it is written having won for it the position of a general favorite. That this high reputation might be fully maintained, the author has subjected it to a thorough revision; every portion has been examined with the aid of the most recent researches in pathology, and the results of modern investigations in both theoretical and practical subjects have been carefully weighed and embodied throughout its pages. The watchful scrutiny of the editor has likewise introduced whatever possesses immediate importance to the American physician in relation to diseases incident to our climate which are little known in England, as well as those points in which experience here has led to different modes of practice; and he has also added largely to the series of illustrations, believing that in this manner valuable assistance may be conveyed to the student in elucidating the text. The work will, therefore, be found thoroughly on a level with the most advanced state of medical science on both sides of the Atlantic.

The additions which the work has received are shown by the fact that notwithstanding an enlargement in the size of the page, more than two hundred additional pages have been necessary to accommodate the two large volumes of the London edition (which sells at ten dollars), within the compass of a single volume, and in its present form it contains the matter of at least three ordinary octavos. Believing it to be a work which should lie on the table of every physician, and be in the hands of every student, the publishers have put it at a price within the reach of all, making it one of the cheapest books as yet presented to the American profession, while at the same time the beauty of its mechanical execution renders it an exceedingly attractive volume.

It would appear almost superfluous to adduce commendatory notices of a work which has so long been established in the position of a standard authority as "Watson's Practice." A few extracts are, however, subjoined from reviews of the new and improved edition.

The fourth edition now appears, so carefully revised, as to add considerably to the value of a book already acknowledged, wherever the English language is read, to be beyond all comparison the best systematic work on the Principles and Practice of Physic in the whole range of medical literature. Every lecture contains proof of the extreme anxiety of the author to keep pace with the advancing knowledge of the day, and to bring the results of the labors, not only of physicians, but of chemists and histologists, before his readers, wherever they can be turned to useful account. And this is done with such a cordial appreciation of the merit due to the industrious observer, such a generous desire to encourage younger and rising men, and such a candid acknowledgment of his own obligations to them, that one scarcely knows whether to admire most the pure, simple, forcible English—the vast amount of useful practical information condensed into the Lectures—or the manly, kind-hearted, unassuming character of the lecturer shining through his work.—*London Med. Times and Gazette*, Oct. 31, 1857.

Thus these admirable volumes come before the profession in their fourth edition, abounding in those distinguished attributes of moderation, judgment, erudite cultivation, clearness, and eloquence, with which they were from the first invested, but yet richer than before in the results of more prolonged observation, and in the able appreciation of the latest advances in pathology and medicine by one of the most profound medical thinkers of the day.—*London Lancet*, Nov. 14, 1857.

The lecturer's skill, his wisdom, his learning, are equalled by the ease of his graceful diction, his eloquence, and the far higher qualities of candor, of courtesy, of modesty, and of generous appreciation of merit in others. May he long remain to instruct us, and to enjoy, in the glorious sunset of his declining years, the honors, the confidence and love gained during his useful life.—*N. A. Med.-Chir. Review*, July, 1858.

Watson's unrivalled, perhaps unapproachable work on Practice—the copious additions made to which (the fourth edition) have given it all the novelty and much of the interest of a new book.—*Charleston Med. Journal*, July, 1858.

Lecturers, practitioners, and students of medicine will equally hail the reappearance of the work of Dr. Watson in the form of a new—a fourth—edition. We merely do justice to our own feelings, and we are sure, of the whole profession, if we thank him for having, in the trouble and turmoil of a large practice, made leisure to supply the hiatus caused by the exhaustion of the publisher's stock of the third edition, which has been severely felt for the last three years. For Dr. Watson has not merely caused the lectures to be reprinted, but scattered through the whole work we find additions or alterations which prove that the author has in every way sought to bring up his teaching to the level of the most recent acquisitions in science.—*Brit. and For. Medico-Chir. Review*, Jan. 1858.

WHAT TO OBSERVE

AT THE BEDSIDE AND AFTER DEATH, IN MEDICAL CASES.

Published under the authority of the London Society for Medical Observation. A new American, from the second and revised London edition. In one very handsome volume, royal 12mo., extra cloth. \$1 00.

To the observer who prefers accuracy to blunders and precision to carelessness, this little book is invaluable.—*N. H. Journal of Medicine*.

One of the finest aids to a young practitioner we have ever seen.—*Pennsylvan. Journal of Medicine*.

WILDE (W. R.),

Surgeon to St. Mark's Ophthalmic and Aural Hospital, Dublin.

AURAL SURGERY, AND THE NATURE AND TREATMENT OF DISEASES OF THE EAR. In one handsome octavo volume, extra cloth, of 476 pages, with illustrations. \$2 50.

New and much enlarged edition—(Now Ready, Oct. 1858.)

WILSON (ERASMUS), F. R. S.,

A SYSTEM OF HUMAN ANATOMY, General and Special. A new and revised American, from the last and enlarged English Edition. Edited by W. H. GOBRECHT, M. D., Professor of Anatomy in the Philadelphia Medical College, &c. Illustrated with three hundred and ninety-seven engravings on wood. In one large and exquisitely printed octavo volume, of over 600 large pages; leather. \$3 25.

The publishers trust that the well earned reputation so long enjoyed by this work will be more than maintained by the present edition. Besides a very thorough revision by the author, it has been most carefully examined by the editor, and the efforts of both have been directed to introducing everything which increased experience in its use has suggested as desirable to render it a complete text-book for those seeking to obtain or to renew an acquaintance with Human Anatomy. The amount of additions which it has thus received may be estimated from the fact that the present edition contains over one-fourth more matter than the last, rendering a smaller type and an enlarged page requisite to keep the volume within a convenient size. The author has not only thus added largely to the work, but he has also made alterations throughout, wherever there appeared the opportunity of improving the arrangement or style, so as to present every fact in its most appropriate manner, and to render the whole as clear and intelligible as possible. The editor has exercised the utmost caution to obtain entire accuracy in the text, and has largely increased the number of illustrations, of which there are about one hundred and fifty more in this edition than in the last, thus bringing distinctly before the eye of the student everything of interest or importance.

The publishers have felt that neither care nor expense should be spared to render the external finish of the volume worthy of the universal favor with which it has been received by the American profession, and they have endeavored consequently to produce in its mechanical execution an improvement corresponding with that which the text has enjoyed. It will therefore be found one of the handsomest specimens of typography as yet produced in this country, and in all respects suited to the office table of the practitioner, notwithstanding the exceedingly low price at which it has been placed.

A few notices of former editions are subjoined.

This is probably the prettiest medical book ever published, and we believe that its intrinsic merits are in keeping with its exterior advantages, having examined it sufficiently to satisfy us that it may be recommended to the student as no less distinguished by its accuracy and clearness of description than by its typographical elegance. The wood-cuts are exquisite.—*British and Foreign Medical Review.*

An elegant edition of one of the most useful and accurate systems of anatomical science which has been issued from the press. The illustrations are really beautiful. In its style the work is extremely concise and intelligible. No one can possibly take up this volume without being struck with the great beauty of its mechanical execution, and the clearness of the descriptions which it contains is equally

evident. Let students, by all means examine the claims of this work on their notice, before they purchase a text-book of the vitally important science which this volume so fully and easily unfolds.—*Lancet.*

In every respect, this work, as an anatomical guide for the student who seeks to obtain knowledge which he has not yet acquired, and for the practitioner who wishes to keep up that which he finds gradually fading from his mind, merits our warmest and most decided praise.—*Med. Gazette.*

We regard it as the best system now extant for students.—*Western Lancet.*

It therefore receives our highest commendation.—*Southern Med. and Surg. Journal.*

BY THE SAME AUTHOR. (Just Issued.)

ON DISEASES OF THE SKIN. Fourth and enlarged American, from the last and improved London edition. In one large octavo volume, of 650 pages, extra cloth, \$2 75.

The writings of Wilson, upon diseases of the skin, are by far the most scientific and practical that have ever been presented to the medical world on this subject. The present edition is a great improvement on all its predecessors. To dwell upon all the great merits and high claims of the work before us, *seriatim*, would indeed be an agreeable service; it would be a mental homage which we could freely offer, but we should thus occupy an undue amount of space in this *Journal*. We will, however, look at some of the more salient points with which it abounds, and which make it incomparably superior in excellence to all other treatises on the subject of dermatology. No mere speculative views are allowed

a place in this volume, which, without a doubt, will, for a very long period, be acknowledged as the chief standard work on dermatology. The principles of an enlightened and rational therapeutics are introduced on every appropriate occasion. The general practitioner and surgeon who, peradventure, may have for years regarded cutaneous maladies as scarcely worthy their attention, because, forsooth, they are not fatal in their tendency; or who, if they have attempted their cure, have followed the blind guidance of empiricism, will almost assuredly be roused to a new and becoming interest in this department of practice, through the inspiring agency of this book.—*Am. Jour. Med. Sciences*, Oct. 1857.

ALSO, NOW READY,

A SERIES OF PLATES ILLUSTRATING WILSON ON DISEASES OF THE SKIN; consisting of nineteen beautifully executed plates, of which twelve are exquisitely colored, presenting the Normal Anatomy and Pathology of the Skin, and containing accurate representations of about one hundred varieties of disease, most of them the size of nature. Price in cloth \$4 25.

In beauty of drawing and accuracy and finish of coloring these plates will be found equal to anything of the kind as yet issued in this country.

One of the best specimens of colored lithographic illustrations that have ever been published in this country. The representations of diseases of the skin, even to the most minute shade of coloring, are remarkably accurate, giving the student or practitioner a very correct idea of the disease he is studying. We know of no work so well adapted to the wants of the general practitioner as Wilson's, with the accompanying plates.—*Med. and Surg. Reporter*, May, 1858.

We have already expressed our high appreciation of Mr. Wilson's treatise on Diseases of the Skin. The plates are comprised in a separate volume, which we counsel all those who possess the text to purchase. It is a beautiful specimen of color printing, and the representations of the various forms of skin disease are as faithful as is possible in plates of the size.—*Boston Med. and Surg. Journal*, April 8, 1858.





LANE MEDICAL LIBRARY

To avoid fine, this book should be returned
on or before the date last stamped below.

--	--	--

QD

30

A141

1854

LANE

HIST

