Edmund O'Neill

A TEXT-BOOK OF
EXPERIMENTAL CHEMISTRY.

(WITH DESCRIPTIVE NOTES)

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A TEXT-BOOK OF
EXPERIMENTAL CHEMISTRY
(WITH DESCRIPTIVE NOTES)

FOR STUDENTS OF
GENERAL INORGANIC CHEMISTRY

BY

EDWIN LEE

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WITH 57 ILLUSTRATIONS

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PREFACE.

WHILE no particular claim to originality is made for this text-book, as many of the experiments have been described previously, yet the writer believes that the book will be found to be something more than a mere compilation. It grew originally out of a personal demand for a text-book which would embody: (a) a clear, accurate and comprehensive presentation of the fundamentals of the science; (b) specific directions for laboratory work, coupled with such questions as lead the student to observe, compare and generalize, and would therefore provide a method for the scientific development of the principles under discussion; (c) a sufficient amount of discussion and application of the principles involved in the experiments to foster the interest and to direct the observations that energy may not be spent indiscriminately, and (d) those physico-chemical generalizations which are essential to the explanation of much of the phenomena of inorganic chemistry.

This book represents an endeavor to meet these requirements. It is not intended that it shall take the place of a large descriptive work or the instruction of the teacher; on the contrary, it is designed to provide, primarily, an experimental course in general chemistry, and by the use of "descriptive notes" and questions *vitally relate* it to the lecture-room work. It is scarcely necessary to emphazise the importance of laboratory work as being essential to a thorough comprehension of the subject; but this same work has a very doubtful value unless it is carefully directed and correlated with the lecture and text-book. It must not be merely a *mechanical* part of the course. The student must see that his laboratory work is but a means to an end—that lectures and experiments are mutually helpful. Very frequently the laboratory work is taught too much *apart* from the course. Beginners often complain, and more frequently conduct their work as if no relation existed between lectures and laboratory work. It is contended, therefore, that the laboratory manual should provide something to make obvious this relationship and to assist in the fusion of the two. It is hoped that the "notes" appended to many of the experiments, and which embody discussions, applications, formulæ, etc., will form the connecting link between the work of the laboratory and the work of the lecture-room. In addition to the foregoing, sufficient amounts of descriptive, theoretical and physical chemistry have been incorporated to present in outline, at least, the essentials of general chemistry. It is presumed, however, that the laboratory work will be accompanied by a full course of lectures.

The *classification* is according to the natural families of the *periodic system.*

The *fundamental concepts* of the science are first built up, explained and illustrated, and then applied persistently.

Neither the *inductive* nor the *deductive* method has been adhered to with "faddish" tenacity. Experience has taught the author that a combination of the two methods can be relied upon to yield satisfactory results. The inductive method possesses undoubted virtues, yet experienced teachers cannot fail to appreciate the pertinency and significance of Faraday's remark, "What are we to look for, Tyndall," as the latter was about to perform an experiment. A too vigorous application of even this method usually results in a waste of energy. There is danger in any extreme. The notes and questions in the book are arranged with a view to imparting definiteness of purpose and aim to the laboratory work.

Most of the exercises have been used in the type-written form for a number of years. They cannot be regarded as "impracticable and beyond the capabilities of the average student." An effort has been made to lighten the labor of the teacher by making the directions *specific.* Further, a series of graduated questions have been incorporated among these directions in order to asisst the student in correlating and generalizing. This also should save the teacher's time and energy. The rigidness imparted by the use of specific directions is overcome by the introduction of abundant material to meet varied conditions—a much larger number of experiments being inserted than will likely be used either in lecture-room or laboratory. This enables the teacher to make a selection.

No hesitancy has been manifested in introducing physico-chemical generalizations wherever they have seemed necessary to rational correlation and explanation of facts. The importance of these generalizations in connection with the teaching of general chemistry is now generally recognized, yet the writer confesses that he knows of no text-book on "experimental chemistry" which has been brought abreast of the times by appropriating and incorporating the results of the labors of the physical chemist. It may be true that physical chemistry cannot and should not be taught in the first year of chemistry, but in the opinion of the author and at least one other, "many of these generalizations which have been brought in by this new physical chemistry, and which affect fundamentally the whole science of chemistry, can and should be introduced into general chemistry." The author would not leave the impression that the older generalizations and methods of developing the subject have been abandoned; on the contrary, they have been retained and an effort made to rationalize them by supplementing them with more recent data taken from the domain of physical chemistry. The book represents, therefore, an effort to fuse modern views and recent advances with those older views which have stood the test, and to explain chemical phenomena in a manner that is in accord with modern chemical thought.

The rôle of energy in chemical reaction has been given unusual prominence. The elements of thermochemistry have been presented. More space has been allotted to "solutions," "the ion theory," "chemical equilibrium" and the "mass law" than is usually given in books of this character. It is believed, however, that the results obtained warrant this. A brief comprehensive statement of the historical development of "the electrolytic dissociation theory" has been given that the student may become familiar with the story of the gradual development of at least one chemical theory. The author has observed that students take a keen delight in stating just how much was contributed to the development of a chemical theory by this or that chemist. With a similar purpose in view, the writer has quoted references *verbatim*, rather than record the gist of them.

Chapter VII presents in outline such subjects as the kinetic-molecular hypothesis, atomic theory, valence, formulæ, equations and units. This gives flexibility to the course by allowing the teacher to develop the several subjects in a manner best suited to the methods in use.

The consulting of easily-found references is demanded frequently. The London *Chemical News* says in this connection: "The habit of looking up whatever needs greater elucidation augurs well for good culture and education." If possible, many of the books mentioned in the reference list should be made accessible to the students.

The author's supreme purpose has been to present a *system* of chemistry rather than an assemblage of chemical facts, and to build a book which will aid the student in cultivating correct habits of thought.

The author acknowledges with pleasure the help and inspiration of those masterful teachers with whom he has been permitted to work.

To his fellow teachers who have been generous with valuable suggestions, he acknowledges his indebtedness. The writer desires especially to thank Professor Arthur B. Lamb, of New York University, and Dr. J. H. Mathews of the University of Wisconsin for helpful criticisms.

For courtesies received, the writer hereby extends his thanks to Professor T. W. Richards of Harvard University, Professor A. A. Noyes and Dr. G. N. Lewis of Massachusetts Institute of Technology, Professor Harry C. Jones and Dr. H. N. Morse of Johns Hopkins University, Professor T. L. R. Morgan of Columbia University, Professor Alexander Smith of the University of Chicago, and Professor F. A. Gooch of Yale University.

I am indebted to my publishers, P. Blakiston's Son & Company, for the use of certain illustrations from several of their publications and desire to express my appreciation of their courtesy.

The author will be grateful to those who report errors and ambiguity.

ALLEGHENY COLLEGE, EDWIN LEE.

Meadville, Penna., June, 1908.

CONTENTS.

INTRODUCTORY.

CHAPTER VI.

CHAPTER VII.

CHAPTER VIII.

CHAPTER IX.

CHAPTER X.

CHAPTER XI.

CHAPTER XII.

CHAPTER XIII.

CHAPTER XIV.

THE NON-METALS OR ACID-FORMING ELEMENTS.

CHAPTER XIX.

CHAPTER XX.

CHAPTER XXI.

CHAPTER XXII.

THE METALS OR BASE-FORMING ELEMENTS.

CHAPTER XXIII.

CHAPTER XXIV.

CHAPTER XXV.

CHAPTER XXVI.

CHAPTER XXVII.

CHAPTER XXVIII.

CHAPTER XXIX.

CHAPTER XXX.

CHAPTER XXXI.

CHAPTER XXXII.

CHAPTER XXXIII.

CHAPTER XXXIV.

CHAPTER XXXV.

LIST OF TABLES.

Heat of Formation

Graduated Solutions:

Percentage and Specific Gravity of Solutions at 15° C.:

LABORATORY INSTRUCTIONS.

After receiving assignment of desk, procure key from rack. Check your apparatus by comparison with list found in drawer. Report any differences *at once* to the assistant.

Read the "Regulations" posted in various places in the laboratory. Always read, in entirety, the directions for performing an experiment before assembling apparatus.

It is well to provide yourself with apron or blouse to protect clothing while at work, also white soft cloth to be used for wiping apparatus. A sponge is convenient.

Procure a note-book (Instructions). Make a neat, permanent and true report of each experiment immediately after its performance under the following heads:

I. Object of Experiment.
II. Manipulation. (What you did.)
III. Observed Phenomena.
IV. Conclusions or Results.
V. Give equations if requested.
VI. Answer questions.
VII. Errata—(any mistakes should be noted under this head).
VIII. A diagram of apparatus frequently facilitates the interpretation of an experiment.

Students must work independently, both as to manipulation and records, unless otherwise specified.

When weighing is necessary, use rough balances unless experiment is marked "Quant."

Do not carry the bottles containing the various substances from the shelves to your desk. Keep the bottles in order. Use a test-tube or watch glass or a piece of paper to transfer substances. Do not return to the bottles unused portions of substances unless you have secured permission from the instructor. If quantity to be used is not specified use 2 $cm.^3$ or 3 $cm.^3$

Do not throw anything away until quite sure that you are through with it. Throw waste liquids into sink; other waste material into waste jars.

When replacing apparatus use order-sheet (pink).

T. O. means that apparatus for experiment is to be secured temporarily from the instructor; *i.e.*, it is to be returned to him after performance of experiment.

L. T. suggests that experiment can be performed to advantage on lecture-table.

Examine your desk on entering the laboratory. If anything has been disturbed or is missing, report same at once to assistant.

Before leaving the laboratory, place your desk in order. Cleanliness is absolutely necessary. Failure to observe this contributes to failure. After observing these instructions, lock your desk and place key on rack. See that gas and water are turned off.

NOTE.—The student will be graded on his "laboratory deportment"; *i. e.*, the persistency with which the foregoing instruct ons are adhered to.

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CHAPTER I.

FUNDAMENTAL CONCEPTS.

RELATIONSHIPS AND DEFINITIONS.

Through the medium of our senses we are constantly receiving sensations which we interpret *objectively*, i.e., we locate the *cause* of a sensation in a particular portion of space. As the result of our experience we assume that the physical universe has an objective existence, and that our acquaintance with it depends solely upon our senses.

Men have given the name **"thing"** or **"entity"** to the *cause* of a sensation—to that which has the objective existence. The entities with which the scientist is particularly concerned are **Matter** and **Energy.** Time, Temperature, Space, Velocity, etc., are not things.*

It will be readily recalled from the student's experience in the study of physics that the two classes of things with which the physicist has to do are those previously enumerated. The same is true of the chemist.

The fundamental difference between Physics and Chemistry rests upon the relative amount of emphasis laid upon either Energy or Matter.

Physics is essentially the science of Energy, and aside from a comparatively brief discussion of the properties of Matter, considers the latter only as it is associated with or becomes "the vehicle of Energy."

Chemistry has been termed the science of matter. This is due to the fact that heretofore but little time has been devoted to energy considerations. Recent years, however, have witnessed a marked change in the methods employed in the study of Chemistry. More emphasis is being placed upon the role of energy in this science. With this change, the artificial line of demarcation, separating Physics and Chemistry, has practically disappeared.

MATTER.

If we consider the evidence furnished by scientific investigation, it is difficult to give a satisfactory and final definition of matter. It is better described by its properties, although it is somewhat evasively defined as anything which occupies space and appeals to the senses. From a

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* NOTE:—A few scientists maintain that there is no such thing as "matter," that it is but an energy manifestation; others hold that neither matter nor energy is an objective reality, but merely a product of thought.

chemical point of view, it has been described as anything which possesses *weight.* Science seems unable as yet to predicate what matter *is.* Experiment has revealed that "the total mass (quantity of matter) of any system is not altered by any process which may take place within that system."—Ostwald. This is often designated as the "law of the conservation of matter." (It is frequently desirable to differentiate the changes occurring within a body or a "set of materials" or a group of bodies from those changes which may take place in its "*surroundings.*" To avoid this cumbrous expression, science has introduced the word "*system*" to designate this assemblage or arrangement of bodies considered as being *insulated* from its environment.)

Definite portions of matter are called **"bodies"** or **"specimens."** Different kinds of matter are called "substances." Bodies may be *homogeneous* or *heterogeneous* accordingly as they are made up of *visibly** like or unlike parts.

Matter appeals to the senses because of its *attributes* or *properties* which are characteristic of a body or a substance.

By the word "property," the idea of a peculiar quality of a thing is conveyed. It implies that which is essential and inherent in a thing, as sweetness is a property of sugar. "The properties of an object are all the relations in which it can be made to appeal to the senses."—Ostwald.

The **identity** of a body or a substance depends upon a definite assemblage of properties.

The matter of the universe is continually undergoing a change, i.e., the properties are being altered in degree or completely changed. Any directly observed change taking place in matter is called a **phenomenon.**

If the change alters the properties of a substance but temporarily, it is said to be a *physical* phenomenon; if the properties are changed permanently, i.e., the substance loses its original identity, the observed change is called a *chemical* phenomenon.

Those properties which are exhibited by physical phenomena are called **physical properties,** and those which require chemical phenomena for their exhibition are called **chemical properties.**

(Physics has sometimes been defined as the study of physical phenomena, and Chemistry as the study of chemical phenomena.)

Physical properties as a class are further subdivided into two groups, **general** and **specific** properties. General properties are those which are possessed in common by all kinds and conditions of matter. Specific properties are those which are characteristic of a particular kind of matter (a substance), yet common to a given *species* of matter. Note that "bodies" cannot always be differentiated from one another by the sole use of specific properties, for if they be "bodies" or "specimens" of one kind of matter, say sulphur, then all the bodies will possess in common the specific properties. Observe that such attributes as size

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* Colloidal solutions represent an exception to this rule if the word "visibly" is used in the ordinary sense of the term.

and form assist in differentiating "bodies," yet said attributes do not enter into our concept of the substance of which the body is composed.

Experiment I.—Matter, Bodies and Substances.

(Record all data in your notebook.)

Place two small pieces of each of the following upon the top of your laboratory desk—zinc, iron, sulphur and glass. How many "bodies" are represented? How many substances? How did you differentiate the bodies? The substances? Name the properties which you made use of in each case.

A piece of sulphur (one cubic cm.), under the ordinary conditions of the laboratory possessed the following physical properties: color, yellow; odor, practically none; hardness, 2.5; melting point, 115° C.; boiling point, 448° C.; specific gravity, 2; specific volume, .5; specific heat, 1.8; insoluble in water; soluble in carbon bisulphide; crystalline structure; opaque; poor conductor; weight, 2 grams; form, cubical; heat capacity, 1.8 x 2; inertia; indestructibility; extension; porosity; impenetrability.

Do all of the properties enumerated above belong to all bodies? To all substances? Classify all of the above properties under the three heads—"general," "specific," and "body" properties.

Which class, or classes of properties enter into your concept of matter? Bodies? Substances?

Can you differentiate bodies by the use of such attributes as weight, form and size? Try to do so by placing the two pieces of sulphur side by side. Can you conceive of any exception to your conclusion? If so, explain.

PHYSICAL PROPERTIES.

Experiment II.—Determination of Specific Gravity. (Quant.)

(*a*) Clean and thoroughly dry a 50 cm.^{3} Erlenmeyer flask; weigh it accurately and record weight of same in your notebook; from a burette containing distilled water at the temperature of the laboratory, measure into flask 10 cm.^{3} of the water. (Recall former instructions relative to meniscus). Weigh as quickly as possible. Calculate the weight of 1 cm.^{3} of water at the temperature of the laboratory. The weight of 1 cm.^{3} of a substance is called its *density.* The weight of the volume of a substance *compared* with the weight of an equal volume of water at the temperature of its maximum density (what is this temperature?) is called its *specific gravity,* i.e., the *ratio* is given this name. The reciprocal of density or specific gravity of a body, or the volume occupied by one gram, is called its *specific volume.*

(*b*) (Quant.) To determine the specific gravity of glass—suspend a piece of silk thread from the hook on the balance and adjust balance so that pointer makes vibrations of equal length on either side of the zero point; tie the thread to the piece of glass so that when a beaker of glass is placed under it, the solid will be completely immersed in the water;

weigh the suspended glass, first in the air and then when immersed. Record the two weights in your notebook. What is the difference in weight? What is the weight of the volume of water equal to the volume of the glass? What is the specific gravity of glass? Its density? The volume of the piece of glass? Its specific volume?

(*c*) (Quant.) Determine the specific gravity of alcohol by means of a specific gravity bottle or an Ostwald-Sprengel pyknometer. (Instructions from assistant.)

(*d*) (Quant.) To ascertain the specific gravity of a solid when only small pieces are available—weigh the specific gravity bottle (Richard's form preferred) when empty; when filled with water and properly arranged; weigh the solid; place the solid in the bottle and add water until bottle is filled, observing all precautions; weigh. Weight of contents? Of solid in bottle? Of water now in bottle? Does the solid displace its own volume of water? What is the weight of this volume of displaced water? Using small pieces of glass, determine its specific gravity.

Experiment III.—Compressibility of Gases.—Boyle's Law. (Quant.)

To determine the relation between volume and pressure. Plot graph of results. (Instructions from assistant.)

Experiment IV.—Expansion of Gases With Increase of Temperature.—Charles' Law. (Quant.) (Instruction.)

Experiment V.—Melting and Boiling Points. (Quant.) (Instructions.) See Traube's "Physico-chemical Methods."

ENERGY.

A body may possess other qualities or "conditions," such as motion, electrical charges or temperature. These conditions may be regarded as energy relations of matter. They do not enter into our concept of a substance, yet their influence upon its properties is very marked in some cases.

Energy is the capacity for work. "It is the essential thing in the universe."—Richards, T. W. By some it has been called the fundamental property of the conceived entity, called "matter." This is probably due to the fact, as science holds, that matter is always associated with more or less energy. The idea of considering energy as a property, thereby subordinating it to matter, is severely criticised by many, who contend that it should be placed on the same plane with matter. The changes in properties and the power to produce them are, therefore, conceived to arise not from a number of distinct entities, but from a single one, which is capable, however, of manifesting itself in a variety of different ways. "That which gives rise to the changes in the properties of bodies and to the power to produce such changes, is called *energy*."—Noyes, A. A.

The familiar forms of energy are, heat energy, light energy, electrical energy, gravitational energy, kinetic energy, etc. Careful experimentation covering a long period of time has shown that equal amounts of the various forms of energy will produce, on transformation, equal amounts of heat. This has led to the enunciation of the law called "*conservation of energy*" which may be stated as follows:

In a limited system, regardless of the transformations which may take place within the system, the total amount of energy is not altered.

Julius Robert Mayer, in 1842, was the first to formulate the above law. It is sometimes called the First Law of Energetics.

The importance of the role of energy in Chemistry gradually becomes more clear as the individual investigates. It is generally admitted that "the existence of matter is inferred only from its various energy manifestations." This leads to the conclusion, that at least so far as our experience is concerned, matter and energy are inseparably connected; that a "body" as we observe it, represents so much of the entity, "matter," associated with more or less of the entity, "energy." Matter * never exists alone, i.e., isolated from energy, and science is quite sure that if the energy were removed from a piece of iron, that its properties would be very different. A body or an object possesses in addition to matter a certain "energy content," which determines its properties. This form of energy, we call *internal energy*. (This does not include kinetic energy.)

Experiment I.—Forms of Energy. Transformation of Energy.

(*a*) Raise the object called a "mortar" from your desk. Did this require energy? Work? What kind of energy did you exert? What kind of energy did you work against? What became of the energy you expended? Was there any energy destroyed in the above operation? Consider yourself and the mortar a body with its capacity for gravitational energy, as constituting a "system;" did the system gain or lose any energy? Was there a *transformation* of energy during the process? State specifically the transformation.

(*b*) Procure a hard rubber or glass rod and a piece of flannel from the assistant; observe that it is somewhat "cold" to the touch and that if touched to pieces of thin paper it does not disturb them; now vigorously rub the rod with the flannel; hold the rod close to the pieces of paper; what is the effect? Touch the rod and note whether it seems to have changed in temperature. The "rubbing" required the expenditure of what kind of energy? It was transformed into what two forms of energy? What bodies constitute our system in this case? Did the system gain or lose energy? Explain. Are chemical or physical phenomena involved in this experiment? Give reason for your answer.

(*c*) Ask the assistant for a d'Arsonval galvanometer, and pieces of iron and copper wires about 20 cm. long. Join the iron and copper wires at one end by twisting them firmly; attach the free ends of the wires to the two binding posts of the galvanometer; take the reading. (Instructions.) Light a match and apply the flame to the juncture (twist) of the two wires; take the reading while applying the heat; this latter form of energy

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* There is much data at hand which points to the conclusion that "matter" is nothing but energy.

is partially transformed into what two forms of energy revealed by the conduct of the galvanometer?

(*d*) (Instructions.) Into a cold dilute solution of hydrochloric acid dip a strip of zinc and a strip of platinum; by means of wires connect strips with the binding posts of an ammeter. Result? Place your hand upon the vessel containing the acid and metals; any change in temperature? Is the zinc being consumed, i.e., is it dissolving in the acid? Has that portion which has been consumed lost its identity, i.e., do you see anything in the acid which seems to possess the same assemblage of properties that zinc possesses? Those phenomena in which there is involved a change of identity of a substance are called *chemical phenomena*. As the result of these *chemical phenomena*, has energy become available for transformation into heat energy and electrical energy? Enumerate as many different forms of energy as you can.

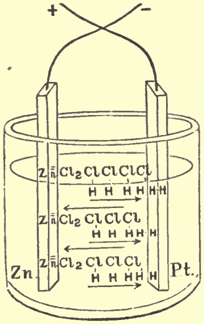

FIG. 1.

From a study of the foregoing experiments the student should readily deduce that energy manifests itself in various forms, many of which are familiar. A form of energy with which the chemist is almost continuously concerned is the one illustrated in the last experiment—the change of identity suffered by zinc when it dissolved in the hydrochloric acid. The zinc strip is supposed to contain a given amount of "zinc matter" and under definite conditions, a definite quantity of energy. It is further asserted that this *internal energy* which is "stored up" in the zinc substance is liberated, at least in part, as "free energy" when the zinc presses into solution, and that it is this so called *free energy* which is transformed into heat and electricity. This relationship of matter and energy will receive attention as we advance in our work.

Experiment II.—Relation of Energy to the Properties of Matter.

(Postulating that our senses can respond to only energy manifestations, proceed with the following experiments.)

(*a*) Procure a cylinder of sulphur (or hard rubber or glass rod) and a piece of flannel from the assistant; examine the piece of sulphur; why does it appeal to the senses? Do these properties bear any relation to energy? (Answer in the light of the above postulate.) If they do not, should properties alter with change of "energy content?" Test your conclusion by experiment; hold the sulphur rod near small pieces of thin paper; has it the property of attracting the paper? Rub the rod vigorously with the flannel; now hold rod near the paper. Is there any alteration or change in the properties of the rod? Did you expend energy in rubbing? If so, what became of it? Explain in terms of energy relations.

Rub the rod again with flannel, supposedly "storing up" an electrical charge on the sulphur; is its energy content thereby changed? Has this changed its identity? Is it possible that many of its properties are altered in so small degree that we are unable to detect the change? Does an alteration in small degree of the properties occasion a loss of identity?

If a small change in the energy condition produces a small change in the properties of a body or a substance as in the case of sulphur, might we be led to assume that great energy changes will be followed by correspondingly great alterations in properties of bodies, perhaps to the extent of changing the identity of a substance, i.e., nearly a complete alteration of properties?

(*b*) Examine the filament in the incandescent lamp over your desk; note its properties as best you can by looking through the glass; observe especially its color, its diameter and its light-giving properties. In view of your previous experience, would you say that the filament possesses a definite amount of internal energy? Does the filament possess a definite assemblage of properties under the present conditions of temperature?

Turn the switch permitting the electricity (energy) to flow through the filament. This energy is transformed into what two forms of energy easily observed? Does the filament contain more or less energy now than when current is not traversing it? Are the properties of the filament altered when the current is flowing through it? Does it lose its identity either temporarily or permanently? Cut off the current, restoring the filament to the original "energy content," i.e., to the same conditions of energy. Does it regain its original properties? If so, what kind of a phenomenon have you been observing?

As the result of this experiment and those which have preceded it, would you feel justified in affirming that there is a *causal* relation between energy and the properties of matter? Should the energy conditions be stated before an attempt is made to describe the properties of a substance? Why?

It seems quite certain that there is a very intimate relation between the properties of a substance and the amount of energy associated with it, that the properties vary in degree as the amount of internal energy varies. It is quite likely, if we could remove the greater portion of the internal energy possessed by sulphur without resorting to chemical processes, that we should have a substance whose properties would be very different from those of sulphur.

The above experiment with the filament of the incandescent lamp emphasizes the fact that when we speak of a substance possessing a particular identity, i.e., a definite set of properties, we mean under certain defined conditions of energy.

Experiment III.—Relation of Energy to Phase of Substance.

Examine several small pieces of ice, it is said to be water in the solid state or *phase*. Has it a definite identity? Place a few small pieces of the ice in a test tube and gently warm the tube and its contents in a flame (heat energy). As long as ice and water are together in the test tube the temperature of the mixture does not alter. What becomes of the energy that is being contributed by the flame? When all of the ice has melted remove the test tube from the flame; you now have water in the liquid phase. Does this same weight of water contain more or less internal energy than the equal weight of ice? Have the properties been altered? If you had never seen water in the liquid phase, would you have recognized it by virtue of your knowledge of the properties of ice? Has the identity of the ice been lost? Introduce the tube and its contents into the flame again, and heat until all of the latter has passed into the gaseous phase. Can you see steam? Does the steam possess more or less internal energy than the water? Are its properties different from those of water, i.e., has the steam an identity of its own? Are these phenomena of a chemical or physical nature? Would you say that the energy content determines, at least in a large measure, the phase or state of aggregation of water? Which phase of a substance has the maximum amount of internal energy?

A solid is frequently said to possess "*form energy*," by which expression we understand that sufficient attraction (cohesive energy) exists among its particles to give it rigidity and form. Because of these attributes due to its energy "condition," a solid is sometimes defined as possessing the properties of specific volume and form. A liquid, possessing less effective *form energy*, has not the property of a definite form, but that of specific volume only. A gas has neither the specific property of form nor definite volume; it possesses relatively the minimum of effective form energy.

When the ice in the above experiment was heated, sufficient energy was imparted to it to overcome the effects of the form energy, at least in part, with the result that the solid was changed into the liquid "state of aggregation." "This latter expression came into use because it is commonly assumed that in the different states, the particles of which a substance is composed, are differently aggregated." Heat energy, when imparted to these particles, acts like a "repellent force" overcoming the form energy and causing a change of state of the substance. A similar course of reasoning is followed in explaining a change from the liquid to the gaseous state.

If form energy is dominant in a substance, then the solid state results; if heat energy is dominant, then the gaseous state prevails.

The energy content of a substance under definite pressure determines its physical state or phase. Considerable confusion has grown out of a careless use of these last two words.

PHASES AND STATES OF MATTER.

If we consider ice, water and water vapor (gas) as constituting a system, then the three *physically* distinct parts of this system represent three *phases*, also three *states*—solid, liquid and gaseous. What is the distinction between "phase" and "state?" Ordinarily we consider but three states of matter, namely, solid, liquid and gaseous, no difference whether we are speaking of and comparing various substances or just one. The word phase is usually defined as a *homogeneous* aggregation or mass. Homogeneous means "like," i.e., possessing same properties; *heterogeneous* expresses the idea of "unlike." If kerosene were poured upon a little water in a test tube and two distinct layers were seen, how many phases would be present? How many states? It is readily seen that we have a mass of water and kerosene which is in the liquid "state," but that we have two phases, i.e., two masses which are each homogeneous. Aggregations of matter which are visibly different or can be mechanically separated from one another are called phases. Examine a piece of granite and there will be visible three kinds of matter physically different, and which can be separated by a mechanical process, hence we have three phases and but one state (solid), represented. The granite is not a homogeneous substance; ice is. The student should remember that the number of different substances present does not necessarily determine the number of phases. When you make a solution of salt and water you have but one phase, because the entire mass is homogeneous. Consider a volume of air; it is composed of many substances, nitrogen and oxygen, chiefly, yet there is but one phase, the gaseous.

Homogeneity must always be the test. The terms phase, homogeneous and heterogeneous are customarily restricted to usage in the physical sense.

Experiment IV.—A Study of Phases of Matter.

Place 5 $cm.^3$ of water in a test tube; how many "states?" Phases? In answering this question ignore air and watery vapor above surface of water. Add 3 $cm.^3$ of alcohol; shake tube well. You have a mass of alcohol and water; is it homogeneous? How many "states" present? Phases?

Repeat above, using kerosene instead of alcohol. Answer above questions in order.

Place 5 $cm.^3$ of water in a test tube; add 2 grams of salt; shake well and heat gently for a few seconds. How many phases? States? Add 5 grams of salt to the solution; treat as before. Do you find that all of the salt will not go into solution? How many states? How many phases?

From the above it is evident that the test of "homogeneity" (used in the physical sense), applied to a mass—solid or liquid—will usually answer the question as to the number of phases present. The *physically distinct* parts of a system represent the phases of it. There is but one phase recognized in the gaseous "state," but many in the solid and liquid states.

CHAPTER II.

CHARACTERISTICS OF PHYSICAL AND CHEMICAL CHANGES.

Those phenomena in which matter undergoes a temporary change of identity, regaining its original identity when the original conditions of energy are again established, are called *physical* changes. When the change in identity is permanent, it is known as a *chemical* change. As a rule, chemical changes are accompanied by physical changes. Chemical changes are defined as those changes which affect the identity, and produce alterations in the substance under defined conditions of energy. Chemistry is primarily the science of these chemical changes and their attendant phenomena.

Experiment I.—Physical and Chemical Changes.

(*a*) Examine the properties of a piece of platinum wire which has been sealed into the end of a glass rod; note its physical properties so carefully that you become sure of its identity. Has it a particular group of properties under the prevailing conditions of energy? Now hold the platinum wire in the Bunsen flame for a few seconds. Note its properties while in the flame. Are they altered? Remove wire from flame, does it continue to glow? Does it emit light now? When you are confident that wire is under the original energy conditions, examine its properties. Has it lost its original identity? What kind of a change did the platinum wire undergo? Define.

(*b*) Note the properties of a piece of magnesium "ribbon;" by means of a pair of pinchers, hold the ribbon in the flame for a few seconds and then remove it; does it give out light and heat after it is removed from the flame? Examine what is left of the ribbon, i.e., the white powder, when it is cooled to the original external energy conditions; has its identity been changed? What kind of a change did the magnesium ribbon undergo? Define.

$$\text{Magnesium} + \text{Oxygen} \longrightarrow \text{Magnesium Oxide.}$$

In the above experiment it must be evident to the student that more energy is yielded by the burning of the magnesium ribbon than was supplied to it by the flame. Is it possible that when it combined with oxygen, they both gave up a quantity of energy which was transformed into heat and light? If so, would the energy content of magnesium oxide be less than the sum of the respective energy contents of magnesium and oxygen?

What kind of changes are illustrated by the rusting of iron, a falling ball, burning coal, melting of ice, and the souring of milk?

Experiment II.—(L. T.) Electrolysis of Water.—Change of Identity.

Make a mixture of acid and water in the ratio of 1 to 20. (Pour the acid into the water slowly.) Fill a Hoffman apparatus (Figs. 2 and 3) for the electrolysis of water with the above mixture. To each of the stop cocks attach a glass delivery tube by means of pieces of rubber tubing, so that they will dip into a vessel of water, a pneumatic trough preferably. Keep stop cocks closed until at least 15 cm.^{3} of gas has collected in the tube which contains the lesser volume of gas. What is the volume in the other tube (approximately)? Now collect in separate test tubes these respective volumes of gases, or portions of them, by "water displacement," i.e., fill a test tube with water and invert it with mouth under water. Open stop cock slowly and gas will be forced through delivery tube, displacing water in test tube. Place your thumb over the test tube mouth under water and bring its mouth upward to a burning match. What happened? Repeat this operation with the other tube of gas. Using a glowing splinter repeat both operations.

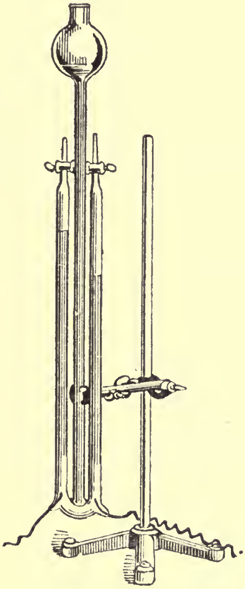

FIG. 2.—Voltameter.

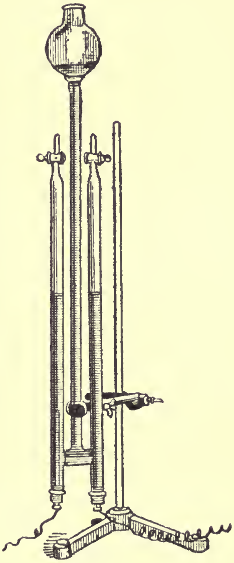

FIG. 3.

The larger volume of gas was *hydrogen;* the other gas was *oxygen* In which gas did the splinter burn most vigorously?

After thus examining the properties of these two gases, would you say that the water has lost its identity?

Water → Hydrogen + Oxygen.

Water is obviously a more complex substance than either hydrogen or oxygen. The water has undergone a chemical change known as *decomposition* or *analysis.*

Experiment III.—Effect of Heat on Mercuric Oxide.

By means of a folded piece of paper introduce a little mercuric oxide (red precipitate) into a dry test tube; determine combined weight of tube and powder by means of chemical balance; note properties of the red powder; heat tube gently. Does color of powder change? Hold a glowing splinter down in the mouth of tube while heating. Results? Do you recall having worked with a gas which revealed similar properties? Its name? Examine the sides of the tube; do they show a metallic luster? What is it? In view of above phenomena what kind of a change would you say you have observed? As the powder in the tube cools does it tend to regain its original color? Is this action the *reverse* of the one which takes place when tube is being heated? Weigh tube and contents. Result?

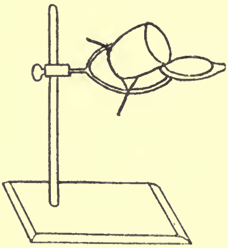

FIG. 4.—(Smith and Keller).

Mercuric oxide ⇄ Mercury + Oxygen.

Of the three substances indicated in the above equation which is the most complex?

The mercuric oxide has undergone what particular kind of chemical change?

Definite conditions of energy seem to be necessary to secure the decomposition of mercuric oxide. Is it possible that the energy contributed by the flame is stored up in the mercury and the oxygen?

Experiment IV.—Effect of Heating Copper in Air.

Clean and dry the small porcelain crucible which you will find in the drawer; introduce into it about 1 gram of powdered copper; by means of chemical balance, find total weight of copper and crucible; place crucible upon a pipe-stem triangle (Fig. 4) and heat with Bunsen flame for 15 to 20 minutes. Is there any change in color? While the crucible and contents are cooling examine the material upon the side shelves, labeled "copper oxide." Does it bear any likeness to substance in crucible? Place crucible and contents upon balance. Have they gained or lost weight? Explain. Which is the more complex, copper, or copper oxide?

Copper + Oxygen → Copper Oxide.

Chemical changes like the one above involving the addition of substances to one another are called *combinations* or *syntheses*. In the experiment, you arranged conditions favorable for the synthesis of copper oxide.

Experiment V.—Solution Facilitates Chemical Action.

(*a*) Place about .5 grm. of tartaric acid in a mortar and pulverize it; add to contents of mortar .5 grm. of sodium hydrogen carbonate (bicarbonate of soda); note that no chemical action takes place; pulverize the mixture; any chemical action? Transfer a little of the powder to a test tube and add water; does a chemical change take place?

(*b*) Add 5 cm.^{3} of concentrated hydrochloric acid to a test tube; add the same quantity of ammonium hydroxide to another tube; hold the mouths of the test tubes near to each other. What evidence of a chemical change? Explain. (Both of the above reagents are gases dissolved in water.)

Chemical action occurring, in which one or more substances are solids, must be largely a *surface phenomenon*, i.e., occurring on the surface. The extent of surface will determine largely the *rate* at which the action proceeds. Substances, finely divided expose more *surface* per unit weight, hence give more intimate contact with one another. Solutions of substances provide a convenient method for securing intimate contact of substances. Gases provide an ideal condition but are bulky and inconvenient to manipulate.

An interesting application of this principle of determining the rate at which the chemical action shall proceed by determining the area of surface exposed, is utilized in the manufacture of explosives. The explosives are cast into cylindrical sticks and the surface is increased by providing a number of longitudinal holes of varying diameters.

Experiment VI.—Relation of Energy to Chemical Change.

From the reagent bottle containing silver nitrate, procure 1 or 2 cm.^{3} of the solution in a clean test tube. Dip the end of the glass stirring rod into the liquid and, using it like ink, write your name upon a piece of white paper; expose the writing upon paper to direct sunlight for half an hour—if need be leave it until next laboratory period. Results? Considering your method of procedure, what factor produced the chemical change?

EXERCISES.

(Record all answers in notebook.)

What form of energy caused the change in the platinum wire? Decomposition of water? Analysis of mercuric oxide? Assisted in the synthesis of copper oxide? Change of silver nitrate? Does energy seem to be as closely identified with chemical changes as it was with physical changes? Has each one of the above changes involved time or have they taken place "instantaneously?" (The word "instantaneously" is seldom found in the vocabulary of a scientist—what do we mean by this affirmation?)

What is the chief distinction from the standpoint of energy considerations between the conduct of the piece of the magnesium ribbon undergoing chemical change and the other chemical changes enumerated above? Was energy necessary to induce the change?

Name the different kinds of chemical changes which you have studied to date.

CHAPTER III.

ELEMENTARY SUBSTANCES, MIXTURES AND COMPOUNDS.

It appears from the foregoing experiments that under suitable conditions of energy, matter can be made to combine with other kinds of matter with little difficulty, producing more complex substances, but it has not been possible to continue simplifying matter indefinitely. It has been impossible to go beyond resolving all kinds of matter into anything more simple than about 80 so-called *elementary substances.* These simple substances have resisted every effort to date to decompose them into anything more simple or elementary. Examples of these elementary substances are, platinum, magnesium, mercury, oxygen, copper, gold, silver, iron, hydrogen. Water is not an elementary substance as you were able to decompose it into two simple substances, namely, hydrogen and oxygen. Substances which can be resolved into something more elementary are not elementary substances. It has been suggested (Richards, T. W.) that this limit to convertibility might be called the "Second Law of Matter."

Experiment I.—Examination of the Elementary Substances.

(L. T.) Ask the assistant to place specimens of the 80 elementary substances on the table, then carefully note the physical properties of the various substances. How many are in the liquid state? Gaseous state? Solid state? Notice flourine, chlorine, bromine, iodine; is there apparently any gradation in properties (physical)?

Observe those which have a metallic lustre. The majority of these are called *metals.* Record the names of those which do not have this property—they are called *non-metals.*

Experiment II.—Energy Content Affects Properties of Elementary Substances.

(L. T.) Compare the properties of yellow phosphorous with those of red phosphorous. Perform such experiments as the assistant suggests. Note: *Don't handle the phosphorus with the hands or take it into the vicinity of much heat; cut it under water.*

The above is a chemical change due to change in energy content, causing a new *internal rearrangement.* Consult lecture notes.

Experiment III.—Mixtures—Heterogeneous and Homogeneous.

(*a*) Try to dissolve a small quantity of flowers of sulphur in water. After shaking vigorously how many phases have you? Can you separate the two substances by a *mechanical* process like filtration (instructions) or evaporation? Did each substance retain its original properties?

(*b*) Dissolve a small quantity of flowers of sulphur in carbon disulphide. (This latter substance is very inflammable and quite poisonous; keep it away from free flames.) How many phases? Pour a little of the solution into a beaker; set it in the open window for 15 to 20 minutes or longer. Results? Does this prove that you had a *mixture?* Why? What kind of a mixture?

A *Mixture* is an aggregate of substances in which each substance retains its characteristic properties. The various substances of a mixture are called "components." One of the best tests of a mixture is, can the substances be separated by mechanical processes.

Experiment IV.—Mixtures and Compounds.

Mix thoroughly in a mortar 5 grams of iron filings and an equal weight of sulphur. Place a portion of the contents of mortar on a sheet of paper and pass a magnet near it. Note that the iron is withdrawn leaving the sulphur.

Introduce a small portion of the contents of mortar into a test tube and add 5 or 6 $cm.^3$ of carbon disulphide; shake tube vigorously; does the sulphur dissolve and leave the iron in the tube? Pour a portion of the liquid upon a watch glass; examine after 15 or 20 minutes. Results? What particular name would you apply to the contents of the mortar?

Now take the portion that remains in the mortar, and by means of a folded paper introduce it into a test tube until tube is half filled; heat test tube to redness. When the iron and sulphur become sufficiently hot they combine and the mass glows brightly although tube is taken out of the flame. (Source of energy?) Cool and break the tube. Examine portions of contents with magnet. Are its properties the same as those of either iron or sulphur? What kind of a change has taken place? The new substance formed is called a *compound.* Did the action continue spontaneously when the flame was removed? Was heat and light liberated as the result of the chemical action?

$$\text{Iron} + \text{Sulphur} \longrightarrow \text{Iron Sulphide}.$$

When elementary substances like iron and sulphur combine to form a new substance whose properties are characteristic, and in which the properties of the combining substances are merged and lost, we say a *compound* has been formed. The various substances uniting are called the "constituents."

All matter may, for purposes of convenience, be divided into three classes, viz.: *elementary substances*, *mixtures*, and *compounds*.

Experiment V.—Interaction of Compounds.

Recall the interaction of hydrochloric acid and ammonium hydroxide.

Experiment VI.—Metathesis—A Species of Chemical Change.

Place a few pieces of potassium iodide in a mortar; observe its color. Now add a small quantity of lead nitrate; observe its properties. Is there any evidence of chemical activity? Pulverize the mass. Is there any indication that a chemical change has taken place? What is it?

This is a case of "double decomposition" or "metathesis." As shown by the following equation, it is a reaction in which the "factors" are represented by one or more compounds and there is an exchange of position between two or more substances.

Potassium Iodide + Lead Nitrate → Lead Iodide + Potassium Nitrate.

Copper + Mercuric Oxide → Mercury + Copper Oxide.

Metathesis is defined as a reaction in which a substance is transferred from one compound to another.

Substances which have a chemical effect on one another are said to *react;* the chemical change is called a *reaction;* the individual substances which participate in the reaction are called *reagents* or "factors;" the new substances formed are called the "products." The properties which enable substances to react on one another with varying degrees of activity are among the more important of what are known as *chemical properties.*

CHAPTER IV.

NOTE ON THE ENERGETICS OF CHEMISTRY.

THEORY.

The importance of the role of energy in its relation to matter, and physical and chemical changes has been obvious in all of the preceding work. The student has become familiar with some of the forms of energy which may be associated with matter; viz., light energy, heat energy, electrical energy, magnetic energy and gravitational energy. (In all the discussions, energy of motion of the body as a whole, i.e. *kinetic* energy, is excluded.) The truthfulness of the First Law of energy has become more apparent. It has been possible to transform energy from one form to another. We know from observation that heat energy supplied by the combustion of fuel, has driven steam engines, which in turn have driven dynamoes supplying electrical energy which has finally been converted into heat energy and light energy. We have understood fairly well this series of energy transformations, but there has been one part which has not been quite so plain, that is, just how and why was heat energy evolved by the combustion of coal in the air? Why was heat energy and light energy developed by the burning of magnesium ribbon in the air, and why should the combining chemically of iron and sulphur manifest similar phenomena? It was not quite plain why heat energy and electrical energy should make their appearance when strips of zinc and copper were properly arranged in a dilute solution of sulphuric acid, although it may have been explained by saying that it was due to the chemical reaction of zinc upon the acid. In all of these cases we failed to observe the presence of any of these familiar forms of energy in or upon the various substances before the chemical action occurred, yet we know that energy was evolved, and that it must have come from some form, possibly some other form of energy in the body of system. (First Law of Energy.)

The question fairly before us is, can we harmonize and interpret these phenomena in the light of our original concept as to the relation of matter and energy? Can we reach some conclusion in regard to the relation which properties, physical and chemical, bear to the "matter content" or "energy content" or both, of various substances?

As was stated in the beginning of the work, matter, as we know it, is conceived of as consisting of an entity, "matter," always associated with a definite quantity of another entity, known as "energy," under defined conditions. For illustration—a piece of the substance iron as we know it, is held to contain so much "iron matter" and so much "internal energy," i.e., any body under defined conditions has a definite "matter content" and a definite "energy content." We can not wholly separate the "energy" from the "matter." What we really see when observing a piece of any substance, is a particular species of matter, simple or compound, associated with a definite quantity of internal energy.

That a very intimate relation does exist between the above two entities is evidenced by the experiments which have been performed. An alteration in the energy content of a body or a system produced certain changes in the physical properties of the substances involved. Many times the physical properties seemed to be sort of functions of the energy content. It was observed also that the energy conditions play a very prominent part in inducing chemical changes. It has been obvious in many of the chemical phenomena, if the Law of Conversation of Energy is universal in its application, that in addition to the change of matter, there has been not only a material altering in the quantity of the *internal energy* of the bodies or systems undergoing such change, but the energy has been frequently transformed.

A more definite conception as to what we mean by the word "internal energy" or "energy content" may aid in an interpretation and explanation of the mechanism of the phenomena all of which at present are not understood.

By the expression *internal energy*, is meant the total energy, regardless of form, *within* a body or system. (This does not include kinetic energy.) In addition to the forms of energy already enumerated, and which may be associated with matter, there are other forms even more uniformly associated with matter, namely, *cohesion energy*, *disgregation energy* and *chemical energy*. The first two are those forms of energy which a body "possesses in virtue of the tendency of its particles to approach and to recede from one another respectively." In solids the *cohesion* energy is relatively greater than the *disgregation* energy; the reverse is true of gases, where the particles tend to repel one another. Elasticity of matter, surface tension, contraction of substances on cooling, etc., all are manifestations of cohesion energy. When a body undergoes change of state by the application of *heat* energy, that which is directly accomplished is the supplying of sufficient *disgregation* energy to overcome, at least in part, the *cohesion* energy. It is evident that the internal energy of the body has been increased, i.e., the energy content is now greater than it was before the change of state. It follows, owing to this relation between cohesion energy and disgregation energy, that if this body after change of state were placed in such a relation that it did not continue to receive heat energy, it would give out heat to its environment and the internal energy would be diminished in amount. Any change in the relation of these two forms of energy in a body will be followed by a change in the internal energy, i.e., heat energy will either be absorbed or evolved. Physical changes, including change of state, receive a comparatively satisfactory explanation by a line of reasoning simila to the foregoing, but not so with the majority of chemical changes. The question might be asked here, what "caused" the magnesium and oxygen of the air to react on one-another? Were cohesion energy and disgregation energy the real "cause" of the reaction? Science says no. Again, was the energy evolved by the combination of magnesium and oxygen exactly equal to the diminution of either cohesion energy or disgregation energy or both, in the system composed of the above two substances? It is true that these two forms of energy may have been altered in degree, but there seems to be another form of energy associated with matter which is probably the main source of energy in the above example, and is possibly the "cause" of the reaction of substances. It is called *chemical energy*, and is possessed by systems in virtue of "this tendency of the substances which comprise the system, to undergo transformations into other substances." The exact nature of this so-called chemical energy has not been determined, but it may be compared with potential energy, for it appears to depend largely if not altogether upon the relative positions of matter in which it resides. An illustration of this is a mixture of hydrogen and oxygen which seems to possess potential energy, because of the proximity of its particles. If a spark is passed through the mixture a chemical change results with the transformation of chemical energy into heat energy. An impulse was required to induce the reaction. (It might be said in a popular way, to overcome "chemical inertia.") This necessity of contributing a small quantity of energy, relatively negligible, to initiate the transformation of energy seems to be characteristic of many phenomena, both chemical and physical. We observed this in the combustion of the magnesium ribbon and in securing the combination of iron and sulphur. Afterwards the reactions proceeded spontaneously. A ball lying at the top of an inclined plane, requires an impulse to start it.

Chemical energy is often regarded as being composed of two factors, one unknown, and the other, possibly, *chemical affinity*. It is obvious that *chemical energy* constitutes but a *part* of the *internal* energy; also let it be noted that in a system (other conditions being the same) where there is considerable tendency of substances to react (affinity) as in the case of hydrogen and oxygen, or magnesium and oxygen, there will be represented more chemical energy, hence more internal energy, than in the case of a system where there is little or no tendency of the substances to react. It is easily seen, then, that if the systems are alike in every other respect, that in the former case, the substances will combine with a greater liberation of energy, due in the main to a transformation of the *chemical* energy. It can not be deduced from this, however, that the diminution in the internal energy of the system, which can be measured, is a measure of the chemical energy or affinity of substances, for it is possible and quite likely that during the chemical change there have been changes in other forms of energy, such as the cohesion and disgregation energies. This latter change would also produce an alteration in the *heat-capacity* of the system which would give it the property to liberate or absorb heat, in degree beyond that which the system originally possessed, exclusive of its chemical energy. Other factors enter also to prevent ordinary usage of the "diminution of the internal energy" of a system as a measure of the "affinity" of substances in the system, but a discussion of same would be out of place in this "note."

The amount of energy available for work, liberated by a body or a system, is called the "*free* energy" (U), while that which is not available to do work is called "*bound* energy." The total energy (internal energy) of a system is equal to the sum of the "free" and "bound" energies. It should not be inferred that because the internal energy of a system is large, that it necessarily follows that the "free" energy content is large. The chemical energy which may be liberated and transformed into free energy from any one substance will differ in amount as it reacts with different substances. When sixteen grams of oxygen combine with hydrogen to form steam about 57,000 calories of heat are liberated; when the same amount of oxygen combines with solid carbon to produce gaseous carbon-dioxide, about 48,500 calories are evolved.

A law of much importance in chemistry is,

That a reaction proceeds in the direction in which there will be the greatest diminution of free energy.

This "free energy" is perhaps most frequently liberated as "heat energy."

Another generalization with which every student of chemistry should be acquainted, and which will enable him to frequently determine the direction of a given reaction when placed under new conditions of energy, is known as Le Chatelier's Theorem.*

"*Any change in the factors of equilibrium from outside, is followed by a reverse change within the system.*"

APPLICATION OF THEORY.

The questions proposed regarding the explanation of various chemical phenomena remain as yet unanswered. What interpretation can we offer from the view point of the foregoing theory? Let us take the case of the combination of iron and sulphur. These are *elementary substances;* they are not *elements.* The word "element" is restricted to mean "matter" alone, as "iron matter," or "sulphur matter." It is an abstraction. We have had no experience with the "elements;" that with which we have experience are the two "elements" associated with their respective and appropriate loads of energy. If the energy could be removed, what would they look like? They each possess a given amount of internal energy (cohesion energy, disgregation energy, chemical energy). The two simple substances were ground together and the mixture placed in a test tube. We conceive of this mixture as constituting a system. Its internal energy is equal to the sum of the energy contents of iron and sulphur. There was no evidence of chemical action, nor anything to indicate the presence of chemical energy, yet when a small quantity of heat energy—an impulse—was imparted to it,

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* Bancroft, The Phase Rule.

the iron and sulphur combined with the evolution of considerable light and heat, to form a compound, known as iron sulphide. The heat and light were the result of the transformation of chemical energy chiefly, with a possbility that a portion was yielded by the transformation of the cohesion and disgregation energies of the respective substances when they passed into the form of the new substances.

The compound (iron sulphide) contains the two "elements" but their energy contents are very different from what they were originally, and therefore we expect the properties of the compounds to be quite different. Is it likely that if we were able to return to the "elements" their original and respective loads of energy that we would secure a return of the elementary substances, iron and sulphur? Consider the decomposition of mercuric oxide. It will be recalled that the reaction continued spontaneously. In most cases where the chemical change proceeds as above to a completion, the free internal energy of the system diminishes by being transformed into other forms of energy. We know that in the combustion of carbon (coal) in air that a very large per cent of the heat of combustion is convertible into free energy (external work).

In concluding this discussion, it might be well to give an example of a chemical change in which there is no apparent alteration in the "matter," the only change being in the energy content. If yellow phosphorous is heated in a closed tube out of contact with the air at a temperature of 250° C., it will be converted into the "allotropic" form known as red phosphorous with an *evolution* of heat.

Yellow Phosphorous.	Red Phosphorous.
Yellow color,	Red color,
Poisonous,	Non-poisonous,
Burns at low temperature,	Burns only at high temperatures,
Phosphorescent,	Non-phosphorescent,
Soluble in CS_2,	Insoluble in CS_2,
Garlic odor,	No odor.

These two substances so different in properties possess in common the "element" phosphorous, but the internal energy of each is different.

Elementary substances, which by virtue of different energy-contents, possess different properties, are called *allotropic.* Other examples are, graphite, diamond and amorphous-carbon.

THERMOCHEMISTRY.

That branch of chemistry which deals with the thermal (heat) changes accompanying chemical reactions is known as **Thermochemistry.** The chief aim of Thermochemistry is to determine the relative "affinities" of different substances by the principle of "the development of the greatest amount of heat." This as ordinarily used furnishes only approximate data.

The principles of thermochemistry are in part summarized by Bloxam as follows:—(1) Every chemical change is accompanied by a thermal change which is a constant quantity. (2) The thermal change occurring during the combination of elements to form a compound is called the *heat* of *formation.** If heat is evolved as it usually is, it is said to be an *exothermic* compound; if heat is absorbed, *endothermic.* Endothermic compounds (usually explosives) contain more internal energy than the constituents originally possessed, and are unstable. (3) The thermal change occurring during the decomposition of a compound is called the *heat* of *decomposition.* (4) The heat of decomposition is identical with, but opposite in sign to the heat of formation of a compound.

The measurement of the thermal changes is accomplished by means of a calorimeter. A very accurate form of this apparatus, known as the "adiabatic calorimeter" has been used for several years in the laboratory of T. W. Richards, of Harvard University.

The two chief laws of thermochemistry are:

The First Law, advanced by Laplace and Lavoisier before the first law of energy had been formulated, states that:

As much heat is given out in the formation of a substance as is required to separate it into its constituents.

The Second Law (Law of Hess)—

No matter how many stages there are in a given chemical reaction, the quantity of heat liberated depends upon the initial and final states.

This is sometimes referred to as the "Constancy of the Heat Sum."

Berthelot proposed a Third Law—

"Reactions go in the direction in which there will be the greatest evolution of heat."

Whereas this has considerable value as a sort of working "rule," it is not to be considered as a law, for it is now known that "free" energy, and not "total" energy, determines the direction of the reaction.

*Note.—The "heat of reaction" is equal to the difference of the sum of the heats of formation of the original substances and the sum of the heats of formation of the final substances—the heat of formation of the elements being counted zero.

CHAPTER V.

SCIENCE—ITS METHODS OF DEVELOPMENT; CLASSIFICATION.

DEVELOPMENT OF SCIENCE.

Men have been led naturally to investigate the causes of the various phenomena observed in the physical universe. As the result of these investigations we have our several sciences.

The initial step in the development of any science is the securing of knowledge by observation and experiment. By an *experiment* is usually meant the process of exhibiting certain phenomena under conditions proposed and controlled by the experimenter. In the conduct of these experiments and in all investigation, we proceed upon the truth of what is now known as a general maxim in physical science—"the constancy of nature," i.e., "like causes produce like effects" and that, irrespective of time and place. The *facts* secured by such procedure, isolated, and apparently unrelated, become the *data* of science. A *fact* is that which has been demonstrated with such accuracy as to leave no reasonable doubt of its truthfulness. As the investigation of nature proceeded, the multitude of facts became cumbersome and unwieldy. Men began to sift this diverse and apparently unrelated *data*, and found much that was common to many phenomena. In the stating of these universal and valid relationships they formulated what are now known as *laws*. After observing the gravitational tendency of many bodies, which observations in themselves constituted *facts*, the universal relationship was recognized and enunciated in the "Universal Law of Gravitation." A *law* is a statement of a constant relation common to a number of phenomena; it is the expression of a relation among facts. "When two substances agree in some few properties they also agree with regard to all other properties." —Ostwald. This statement of the relationship, as a summary of observed facts, is called a *law*. It makes no endeavor to explain. The student should understand that "it does not govern or state what will happen; it predicates an invariable relation."—Nernst. There are no exceptions to laws; if there is an exception to a law it is no law. The word "rule" has been frequently confused with the word "law" in this latter sense. A "*rule*" is merely a statement of the usual order of events —the customary procedure and condition of things, as, the earth turns upon its axis once a day. "Exceptions to rules do not destroy them as rules, in fact we say 'the exception proves the rule.'"—Richards, T. W.

It is interesting to note the two methods by which these relationships have been discovered. When the individual, by experiment and observation, gathers data concerning phenomena among which he suspects a relationship, and arranges it empirically and then endeavors by *experiment* to verify his suspicions, he is said to resort to the *inductive method*, sometimes called the *empirical method.*

The other method used in an endeavor to discover relationships is known as the *deductive or theoretical method*, and is largely a mental process. It consists in starting with merely a conception regarding the relations among phenomena, then by pure speculation to make new deductions, which must be verified by research.

The *inductive* method leads us to definite and usually reliable results.

The *deductive* method is more fascinating and enables us to penetrate more deeply into the relationships, but we must be very careful and cautious in the choice of the original concept which many times can not be verified by a *direct* test.

Conceptions of this kind which can not be directly verified are called *hypotheses.* The imaginative element predominates in these concepts which are mere *assumptions* of "the existence of conditions of which we can have no direct experimental evidence." An *hypothesis* is an effort to explain the mechanism, the "why" of certain phenomena, and to correlate same, that from this *general* proposition new conclusions may be drawn. This new body of conclusions constitutes a *theory*, which should be tested by experimental methods. A *prediction* is merely a guess and can be tested.

In this connection our attention is called to the *scientific* and *systematic* methods—the two being commonly confused, although they are entirely distinct. *Science* consists in discovering the laws to which phenomena conform and is exemplified by such studies as chemistry, biology, mathematics and similar analytical studies. *System* consists merely in the classification of phenomena as illustrated by grammar, history, etc. Natural history preceded biology, the former merely classified; the latter has become a true science by the introduction of analytical ideas of the relations of heredity, environment, etc. Many systematic studies have now given away to the truly scientific.

CLASSIFICATION OF SCIENCE.

In the course of time knowledge became so extensive and diverse that it was evident that the great bulk of related knowledge which might properly be called Natural Science must be divided for convenience into a number of more limited ones. These various divisions of the one large study or science are called the "natural sciences." The distinction between "living matter" and "non-living matter" is made the basis for a division of these natural sciences into two great groups known as the *Biological Sciences* and the *Physical Sciences.* The Biological Sciences deal with matter in the living condition, while the Physical Sciences has to do primarily with matter in the lifeless condition.

Matter.

- **I.** Organic—Biological Sciences.
  - A. Biology (general).
    - a 1. Botany.
    - a 2. Zoology.
- **II.** Inorganic—Physical Sciences.
  - A. Physics and Chemistry.
    - a 1. Astronomy (Physics of the heavens).
    - a 2. Meteorology.
    - a 3. Geology, etc.

As will be observed from the above outline it is possible to extend our original classification into what are known as the General or Speculative Sciences and the Special or Descriptive Sciences. Physics and Chemistry occupying themselves with the study of general properties and "transformations" of bodies regardless of external form, and dealing with the substance only, are called the Speculative or General Sciences. Geology, Astronomy, Meteorology, etc., considering distinct classes of *bodies* in reference to form, classification and distinguishing characteristics, are known as the Descriptive or Special Sciences.

Chemistry is a descriptive science in so far as it considers the external properties of chemical substances.

Again all knowledge may be gathered under the respective headings of the Abstract Sciences and the Concrete Sciences.

The *Abstract Sciences*, including logic, mathematics, etc., are not concerned primarily with matter, but with abstract conceptions. The *Concrete Sciences* are concerned with bodies, i.e., "definite aggregation of matter," whether living or lifeless. Zoology, Astronomy, etc., would be included under this head. Physics and Chemistry, having to do with both the abstract and the concrete, are frequently named the "abstract-concrete" sciences.

CHAPTER VI.

QUANTITATIVE RELATIONSHIPS.

LAWS AND CHEMICAL EQUIVALENTS.

As a science progresses in accuracy it progresses in the true scientific spirit. We have been led to the conclusion in the foregoing work that definite quantities of any substance under defined conditions possess a definite quantity of internal energy. The question might rise logically, as to whether the "factors" and "products," as referred to matter, involved in a chemical change bear any such definite relation to one another, that is, when substances combine to form new compounds, (a) does the matter in the system sustain an appreciable loss or gain, (b) do the reacting substances combine in any definite ratio by weight or volume, (c) do the constituents of the new substance bear to one another a fixed ratio by weight or volume, (d) does variation in the conditions cause a variation in any possible ratio in which substances may combine with one another? To aid us in understanding the conclusions which have been reached in regard to these questions, as the result of much patient and painstaking labor, let us perform a series of experiments.

Experiments are of two kinds, *qualitative* and *quantitative*. The former are resorted to in order to illustrate a property or group of properties. We consider only *what* takes place. Quantitative experiments, for example, accept the fact that gases are compressible, then endeavor to determine the exact amount of compressibility for each increment of pressure. They seek to determine any possible mathematical relation of cause and effect.

Experiment I.—Conservation of Mass.

(*a*) (L. T.)—Analysis of Water. Counterpoise an electrolysis apparatus upon a scale pan, or better, fit a rubber stopper containing three holes into a 250 cm.^{3} flask; half fill the flask with water slightly acidulated with sulphuric acid; insert two electrodes through holes in cork, reserving third hole for a glass tube with rubber tubing and pinch cock attached; by means of this latter and an air-pump exhaust air above water from flask; close pinch cock; invert flask; mark height of contents; counterpoise apparatus on balance; turn on the electric current; note bubbles of gas arising from electrodes. Caution: Don't continue process of decomposition too long. Counterpoise apparatus again; any gain or loss in weight? Is the sum of the weights of the "products" equal to the sum of the weights of the "factors?"

$$\text{Water} \longrightarrow \text{Hydrogen} + \text{Oxygen}.$$

(*b*) (L. T.)—Synthesis of Water. Perform this operation by means of a Hoffman eudiometer (Figs. 5 and 6). Introduce into apparatus about equal volumes of hydrogen and oxygen; observe volume of the mixture of gases.

Note.—It is well to use an excess of one or the other of the gases so that when the contraction of volume of gases occurs, there will be a cushion of gas between top of glass tube and the mercury. What deductions, as regards the relation of products and factors, can you make?

Hydrogen + Oxygen → Water.

As the result of much refined work it has been concluded that regardless of chemical change there is "conservation of mass" in a limited system. It is quite possible that Van Helmont (1577–1644) was acquainted with the principle. The law was first enunciated by Lavoisier (1789). It is commonly spoken of as the law of the "indestructibility of matter."

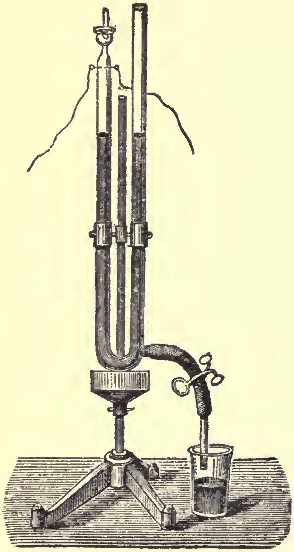

FIG. 5.

Experiment II.—Combination in Definite Proportions by Weight.

(*a*) Synthesis of copper oxide. Clean and dry a small porcelain crucible; weigh it; put into it about 1 gram of powdered copper; secure the exact weight; place crucible on pipe-stem triangle which may be supported by tripod or ring clamp. Heat crucible and contents to redness in a Bunsen flame for fifteen minutes; remove flame and let crucible cool; weigh; make record of weight. Repeat operations until weight becomes constant.

Copper + Oxygen → Copper Oxide.

Tabulate your data as follows:—

Weight of crucible and copper	0.000
Weight of crucible	0.000
Weight of copper	0.000
Weight of crucible and copper before heating	0.000
Weight of crucible and copper, after heating	0.000
Weight of oxygen, combined with copper	0.000

FIG 6.
Eudiometer.

Calculate how much oxygen would combine with a gram of copper. What is the ratio of the combining weights of copper and oxygen under above conditions? What is the class average?

(*b*) Optional. Synthesis of magnesium oxide. Prepare crucible and cover as above; weigh into it about 300 mg. of magnesium ribbon; use forceps and scissors for manipulation of ribbon; make a record of the exact weights as above. Place covered crucible on triangle and cautiously heat it to a dull redness—then quickly removing flame, raise cover of crucible and observe whether the magnesium starts to glow, which is desired,—if it does, quickly replace cover so that none of the magnesium oxide escapes. This operation of heating to redness, removing flame and lifting cover must be repeated until a constant weight is secured and the contents of crucible have a white or grayish color. Tabulate data and calculate ratio of combining weights as in (*a*).

Magnesium + Oxygen → Magnesium Oxide.

(*c*) Optional. Synthesis of iron oxide. Pure iron wire dissolved in nitric acid gives a compound which on being heated sufficiently, is converted into iron oxide. Into a thoroughly cleaned and dried evaporating dish which has been weighed, introduce about 750 mg. of iron wire. (Instructions.) Record exact weight of wire used. Place cover glass on dish; add 10 $cm.^3$ of dilute nitric acid. Now fill a beaker nearly half full of water and heat the water until it boils vigorously; place covered evaporating dish on beaker so that the latter serves as a steam bath; keep cover on until all of the iron wire has dissolved, then remove cover and evaporate to dryness; the direct flame may now be applied to the dish; continue its use until a constant weight is secured. As long as red fumes are observed rising from the dish, it will be unnecessary to cool and weigh. The powder remaining in dish is iron oxide. Tabulate data and calculate as in (*a*). What is the ratio of the combining weights?

It is quite obvious in these experiments that we have not been able to get substances to combine in any promiscuous ratio; on the contrary the combining substances have united in certain fixed ratios by weight. A generalization of this principle is known as the "Law of Definite Proportions." It was practically confirmed and announced by Proust in 1806, and came largely as the result of a controversy between Berthollet and Proust. The law as frequently stated is,

The same compound always contains the same elements combined together in the same proportion by weight.

Experiment III.—Constancy of Composition.

Liberation of oxygen by decomposition of potassium chlorate.

Note.—A small quantity of potassium chlorate may be heated in a test tube and the evolved gas tested for oxygen.

Clean and dry and heat a porcelain crucible and lid; cool in a desiccator; weigh accurately and record weight; introduce into the crucible an accurately weighed quantity, say 1.2 gram, of powdered potassium chlorate which has been previously dried at a temperature of about 100° C. for 15 to 20 min. Place crucible and contents on a pipe-stem triangle and heat gently in order to prevent spattering; if any of the salt is deposited upon the cover, the latter must be cooled, and the salt returned to crucible. When the mass solidifies and action has apparently stopped, increase the heat until a perfectly white, non-crystalline mass which is not altered by a further increase of heat, results. Remove cover and heat strongly for a few minutes; cool in desiccator and weigh as before. Record weight. Heat again for 10–15 min.; cool; weigh. Repeat until weight is practically constant. Tabulate all data as in a previous experiment. Calculate the percentage of oxygen in potassium chlorate.

Above result indicates in the case of this compound, potassium chlorate, that a definite proportion by weight of oxygen can be secured from a definite weight of the compound. Further experimentation confirms this principle, known as the "law of constancy of composition." It is but a special statement of what law?

Experiment IV.—Combination of Two Substances in Varying Proportions by Weight.

(*a*) Optional. Synthesis of mercuric iodide ($Hg\ I_2$), as compared with synthesis of mercurous iodide (Hg I). (Instructions from the assistant.)

(*b*) A qualitative experiment designed to show in a general way the difference between the properties of two compound substances, each of which is composed of the same elementary substances but in different proportions by weight. Synthesis of nitrogen dioxide ($N_2\ O_2$) as compared with the synthesis of nitrogen tetroxide ($N_2\ O_4$). Assemble parts of a gas generating flask equipped with delivery tube; place about 10 grams of copper turnings in the flask; arrange delivery tube so that it dips into a vessel of water (pneumatic trough). Pour through the funnel tube about 15 $cm.^3$ of nitric acid diluted with its own volume of water, then add a few $cm.^3$ of concentrated nitric acid at a time until there is a rapid evolution of gas; after gas has been evolved for a few minutes collect several bottles of the *colorless* gas by water displacement; place a glass plate or a piece of wet paper over mouth of bottle on lifting it from water; remove cover so that oxygen of air can come into intimate contact with the colorless gas. Does the gas in the bottle become brownish-red in color? The colorless gas is a combination of nitrogen and oxygen in the ratio by weight of 14 to 16; the brownish-red gas is composed of the same gases but in the ratio by weight of 14 to 32. Were the conditions under which two compounds formed identical? Explain.

This is an illustration of the "Law of Multiple Proportions."

If two elements unite in more than one proportion, forming two or more compounds, the different weights of one of the elements, which in the different compounds are united with identical amounts of the other, bear a simple ratio to one another.

It is not an exception to the law of definite proportions which applies to either one of the compounds formed. The conditions under which each compound was formed were different. See under "Copper."—Exp., Preparation of Cuprous and Cupric Chlorides.

Experiment V.—Combining Volumes of Gases.

(*a*) Synthesis of water from hydrogen and oxygen gases. Introduce 30 cm.^{3} of each of the two gases into a Hoffman eudiometer, U-form (Fig. 5). Observe proper precautions to collect gases at atmospheric pressure. Open lower stop cock permitting some of the mercury to run out, thus allowing gases to expand; pass spark, and then bring mercury columns to same level. Read. Repeat using 25 cm.^{3}; 20 cm.^{3}, of each gas. Record all data. What is the average of the ratios of the combining volumes?

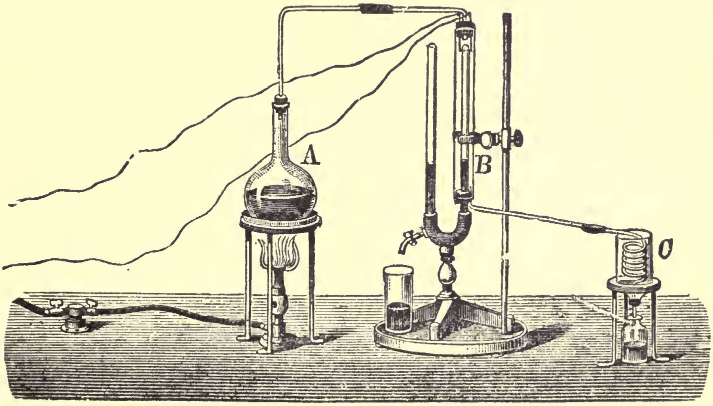

FIG. 7.

Note.—Before passing spark through mixture of gases it is well to place thumb on open tube to prevent the mercury from being forced out.

(*b*) Synthesis of steam from hydrogen and oxygen gases.

Introduce 25 cm.^{8} of each of the two gases into an eudiometer (Fig. 7) which is inclosed in a glass tube which may serve as a steam jacket; the eudiometer should be connected with a leveling bulb and the gases collected over mercury; the gases must be perfectly dry, as should the mercury; after gases have been collected, pass steam through jacket until entire system is at the temperature of steam; observe volume of mixture of gases when mercury in eudiometer is at same height as it is in the leveling bulb; lower leveling bulb permitting gases to expand; clamp tubing below eudiometer; pass spark through mixture of gases; bring mercury columns to the same height again; note volume. Deduct one-fourth the volume of the mixture of gases at 100° C. from this final volume (Why?). What relation does this volume bear to three-fourths of the volume of the mixture of gases at the temperature of the steam?

Note.—If more desirable to teacher, the exact combining volumes may be used as prepared by electrolysis of water.

Experiment has shown that two volumes of hydrogen gas combine with one volume of oxygen gas to produce water. Further it has been shown that when the quantity of water has been converted into steam, that its volume is to the sum of the combining volumes of hydrogen and oxygen at the same temperature, as 2 to 3.

These and similar experimental results have given rise to a law, known as the "Law of Gaseous Volumes" or "The Law of Gay-Lussac."

When chemical action takes place between gases, either elements or compounds, the gaseous product bears a simple relation to the volume of the reacting gases.

A relationship which may be noted at once by a study of the foregoing experiments is stated as the Law of Reciprocal Proportions, or Law of Equivalent Proportions.

The weights of different elements which combine separately and with one and the same weight of another element, are either the same as or are simple multiples of, the weights of these different elements which combine with each other.

It might be called the "law of inter-equivalence of equivalent weights." An application of this principle may be made as follows:—63.6 parts by weight of copper or 24.3 parts by weight of magnesium combine with 16 parts by weight of oxygen; 2 parts by weight of hydrogen also combine with 16 parts by weight of oxygen; therefore, it is obvious that 63.6 parts of copper, 24.3 parts of magnesium and 2 parts of hydrogen are *chemically equivalent*, that is, these proportions by weight satisfy the chemical affinity of one another. Again it is to be observed that 1 part by weight of hydrogen is *chemically equivalent* to 31.8 parts by weight of copper, 12.2 of magnesium, and 8 of oxygen. Inasmuch as hydrogen, the lightest of all elements, has the smallest combining weight, Dalton proposed to make this weight the standard, and express all combining weights in terms of it. Berzelius proposed oxygen, which is about 16 times as heavy. These weights of elements which are chemically equivalent to 1 part by weight of hydrogen are called *chemical equivalents*. More accurately, that weight of an element which combines with or displaces 8 parts of oxygen or 1.0075 parts of hydrogen by weight is called the *equivalent weight*. Specifically, *it is the number of grams of an element which combines with or replaces* 1.0075 *grams of hydrogen or* 8 *grams of oxygen.*

If the student finds this word "*equivalent*" difficult to understand in this connection, some satisfaction may be secured by knowing that this same word delayed the development of chemical theory many years.

Experiment VI.—Equivalent Weight of Zinc by Displacing of Hydrogen.

See Exp. under "Hydrogen."

CHAPTER VII.

OUTLINES.

THEORIES, FORMULÆ, VALENCE, EQUATIONS AND UNITS.

Structure of Matter.—Continuous or discontinuous? Matter bears evidence of possessing a *granular* structure.

Statement and Historical Development of the Kinetic-Molecular Hypothesis.

Definitions of a Molecule.

(1) A molecule is the smallest particle of matter which can exist alone and retain the properties of a substance.
(2) "Molecules are the imaginary units of which bodies are the aggregates."—Smith.
(3) A molecule is the physicist's unit.*

Application of Kinetic-Molecular Hypothesis to,

(1) Solids,
(2) Liquids,
(3) Gases.
    Boyle's Law.
    Charles' Law (Dalton—Gay-Lussac—Charles).
    Avogadro's Rule.
    Gas Law ($PV = RT$).

Critical Phenomena.—Experiments with "critical" tubes.

(*a*) Critical Temperature (H,—238° C.), (O,—118° C.), (Ether, 195° C.).
(*b*) Critical Pressure (H, 20 atmos.), (O, 51 atmos.), (Ether, 36 atmos.).
(*c*) Critical Point.
(*d*) Critical Volume.

Combining Volumes.—Recall Exp. and Law as discussed under "Quantitative Relationships." Two volumes of hydrogen, say 40 cm.^{3} combine with one volume, 20 cm.^{3} of oxygen to form two volumes, 40 cm.^{3} of steam (water).

□ □ + □ → □ □
2 Vol. Hydrogen. 1 Vol. Oyxgen. 2 Vol. Steam.
(1 molecule of oxygen must divide.)

□ + □ → □ □
Hydrogen. Chlorine. Hydrogen Chloride.
(Both molecules must divide.)

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* The modern physioist will probably insist that the "electron" is the unit.

Statement and Historical Development of Atomic Theory.

Definitions of an Atom.

(1) An Atom is the smallest particle of matter which can participate in a chemical reaction.
(2) Atoms are the imaginary units of which molecules are the aggregate.
(3) An atom is the chemist's unit.
(4) An atom always represents a distinct variety of matter.

Statement of J. J. Thomson's Electronic Theory of Matter. See Thomson's "Electricity and Matter."

Application of Atomic Theory to,

(1) Chemical Reaction.
(2) Quantitative Relationships.

Atomic Weight *"is the number which represents the smallest mass of an element which is known to participate in a chemical change, relative to the smallest weight of hydrogen which can so function"*—Newth; or, *"it is the unit of weight actually used in expressing the proportions of each element in all of its compounds."*—Smith.

Note.—Hydrogen has been practically abandoned in favor of oxygen as the standard of atomic weights.

Nomenclature of Atomic Theory.

Symbols (Hg, O, H, etc.).
Molecular Formulæ.
(*a*) Simple Molecules (H_2, O_2, O_3, Hg, As_4, S_8).
(*b*) Compound Molecules (FeS, HgO, H_2O, HCl, MgO).

Molecular Weight *is equal to the sum of the atomic weights of all of the atoms of which the molecule is composed.*

DETERMINATION OF MOLECULAR FORMULÆ AND EQUATIONS.

Equations.—

(*a*) Matter or Mass Equations.

EXAMPLES:

$$H_2 + O \rightarrow H_2O.$$
$$H_2 + Cl_2 \rightarrow 2HCl.$$
$$Mg + O \rightarrow MgO.$$

(*b*) Energy Equations.

EXAMPLES:

$$H_2 + O \rightarrow H_2O + 68{,}000 \text{ cal.}$$
$$H_2 + Cl_2 \rightarrow 2HCl + 44{,}000 \text{ cal.}$$
$$C + O_2 \rightarrow CO_2 + 97{,}000 \text{ cal.}$$
$$H_2 + I_2 \rightarrow 2HI - 12{,}000 \text{ cal.}$$
$$Hg + O \rightarrow HgO + 22{,}000 \text{ cal.}$$

When a body or substance, by virtue of its position or its motion or its state, is capable of doing work it is said to possess energy; if resistance is overcome, work is done. Atoms do not exist as individuals except in a few instances (Hg, Na, K, Zn, Cd, He, A, Kr, Ne, X); they are united to form molecules, simple or compound, of varying degrees of stability. The stability of this equilibrium is evidently determined by some force operative between the individual atoms; for want of a better term we designate this force "chemism" or "chemical affinity" (see Note on Energetics of Chemistry). To return to our original line of thought, it is evident that atoms possess energy, because in uniting they are capable of performing work. Atoms are said to possess "chemical energy" (see Note on Energetics of Chemistry) in virtue of their tendency to combine with other atoms.

It is probable that the energy liberated when atoms combine is due to a transformation of all or a part of this chemical energy into *free energy*, i.e., energy which is available for the performance of work. If certain kinds of atoms have a great chemical affinity for one another they, that is the system which they represent, possesses a large amount of chemical energy which will probably be converted into a correspondingly large amount of free energy. Molecules formed under such conditions possess much smaller quantities of energy than their constituent atoms originally possessed, consequently they are stable. Again, two or more atoms may possess so very little chemical affinity for each other that it will be necessary to contribute energy to secure their combination; molecules formed under these conditions will have a tendency to convert this acquired energy into free energy and therefore, will be unstable.

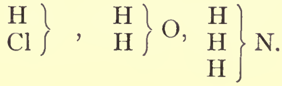
The atoms of the elements show great variations in respect to the chemical affinity which they manifest toward one another; the same is true as regards the interaction of groups of atoms.

Valence, or Quantivalence *is the atom fixing or replacing power of an atom of an element in terms of the hydrogen atom which is considered as having a valence of one.* Those atoms which have a valence of one, two, three, etc., are said to be respectively *univalent*, *bivalent*, *trivalent*, etc.

Multiple Valence.—The valence of an elementary atom "*is not an invariable property of the atom, but each of the observed differences as to its valence is an invariable property of some particular condition of the atom dependent on the circumstances in which it is placed.*"

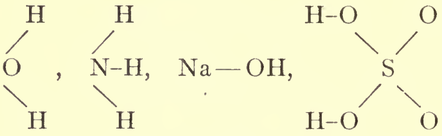
Formulæ.

Empirical, Ex., H_2O, $C_2H_4O_2$.
Rational, Ex., $HC_2H_3O_2$.
Dualistic, Ex., $H_2O.SO_3$, $Na_2O.SO_3$, $Na_2O.H_2O$.

Typical,


$$\left.\begin{matrix}H\\Cl\end{matrix}\right\}, \quad \left.\begin{matrix}H\\H\end{matrix}\right\}O, \quad \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N.$$

Structural or Graphic,



Space (formulæ of more than one dimension, to represent the configuration of a molecule).

Units of Measurement.

Length—Cm., mm.
Volume—$Cm.^3$, liter.

Weight.
- (*a*) Gram.
- (*b*) Gram-molecule (mole).
- (*c*) Formula-Weight.

Temperature—Centigrade Scale.
- (*a*) Boiling Point (100° C.).
- (*b*) Freezing Point (0° C.).
- (*c*) Absolute Zero (—273° C.).

Heat Units—Calorie.
- (*a*) Small Calorie.
- (*b*) Large Calorie.
- (*c*) Ostwald Calorie.

Calculations in Chemistry (Stoichiometry).—Problems.

$Mg + O \rightarrow MgO.$
24 16 40.
$KClO_3 \rightarrow KCl + 3O.$
122.5 74.5 48.

DETERMINATION OF MOLECULAR AND ATOMIC WEIGHTS.

Methods.

(1) Volumetric.—(Molar-volume 22.4 l.).
(2) Chemical.
(3) Specific Heats—Atomic Heat.
  Dulong and Petit's Law—Neumann's Rule.
(4) Isomorphism.
(5) Elevation of Boiling Point.
(6) Depression of Freezing Point.

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Elevation of Boiling Point, etc.—Physical Chemistry.—Walker. Physical Chemistry.—Jones. Theoretical Chemistry.—Nernst. Modern Theory of Solution.—Jones. See later work under the subject of "Solutions."

PROBLEMS.

Note.—See At. Wt. tables in Appendix.

1.—What is the molecular weight of HgO, H_2O, FeS, MgO, HCl, H_2SO_4, HNO_3, NH_4OH, $NaOH$, KOH?

2.—$Mg + O \longrightarrow MgO$. 5 grams of magnesium will combine with how many grams of oxygen? Now many grams of magnesium oxide will be formed?

3.—How many grams of hydrogen in 10 grams of H_2O?

4.—How many grams of oxygen can be prepared from 10 grams of mercuric oxide? $HgO \longrightarrow Hg + O$.

5.—$Fe + S \longrightarrow FeS$. If 10 grams each of sulphur and iron are placed in the test tube and chemical action results with a transfer of all of the iron into iron sulphide, how much sulphur remains in the uncombined condition?

6.—How much oxygen can be prepared from two gram-molecules of potassium chlorate? $KClO_3 \longrightarrow KCl + 3O$.

7.—A certain weight of $KClO_3$, was heated until completely decomposed as per above equation. The residue weighed 10.123 gm. What was the original weight of $KClO_3$, and how much oxygen was evolved? How many liters of oxygen were liberated if the standard weight of a l. of oxygen is 1.4 gm.?

8.—At 760 mm. and 0° C. how many liters of gas in 2 gm. (molecular wt.) of hydrogen? In 16 gm. (.5 mol. wt.) of oxygen? In 32 gm. (mol. wt.) of oxygen? What is the molar volume?

9.—(*a*) 5.6 l. of a gaseous substance weights 4.5 gm. approximately, at standard conditions; what is its molecular weight?

(*b*) If $\frac{1}{9}$ by weight of this substance is hydrogen and $\frac{8}{9}$ oxygen, what is its formula?

10.—(*a*) If the specific heat of Ag (silver) is approximately .057, what is its atomic weight? Of Fe, if sp.ht. is .112?

(*b*) If the sp.ht. of Ag Cl (silver chloride) is .089, prove that the atomic weight of Cl is nearer 35 than 70. What is the atomic heat of chlorine?

11.—Write the structural formula for NH_3, H_2O, MgO, FeS, HCl, and H_2SO_4, if in this latter compound (sulphuric acid) sulphur has a valency of 6.

CHAPTER VIII.

OXYGEN.

Symbol—O. At. Wt. 16 (15.9).

Oxygen is an elementary substance belonging to the class previously designated as "non-metals." It was first discovered by Priestly, who in 1774 prepared it "by heating 'red precipitate' (red oxide of mercury) in the focus of a burning glass exposed to the sun's rays." It is quite probable that Scheele, a Swedish chemist, had previously obtained it, but he delayed publication of his results until 1777. Lavoisier, a French chemist, named the new element "oxygen" which signifies acid-producer. He believed that all acids owe their characteristic properties to the presence of oxygen. Cavendish pointed out that many substances which do not contain oxygen possess acid properties. We now know that Lavoisier's view was incorrect.

Occurrence.—Oxygen is the most abundant element upon our planet; it forms about 47 per cent. of the solid portion of the earth and constitutes 20 per cent. of the earth's atmosphere. Including its occurrence in the ocean, vegetable and animal forms, etc., it constitutes 50 per cent. of the total substance of the globe. It occurs most abundantly in the *free* state in the air.

Physical Properties.—Oxygen is a colorless, odorless and tasteless gas; it is slightly heavier than the air; its density as compared with air which is considered as 1 (physical standard), is 1.105. One liter of oxygen at standard conditions weighs 1.429 gm. It is slightly soluble in water, 100 volumes dissolving 4.1 volumes of oxygen at 5° C. Its critical temperature is —118° C.; its critical pressure, 50 atmospheres. Liquid oxygen boils at —182° C. at 740 mm. pressure (Dewar and Fleming); it has a pale-blue color; its sp. gr. at 182.5° C. is 1.13.

Chemical Properties.—By chemical properties is meant "*reaction properties.*" Oxygen possesses an almost universal affinity, i.e., "it forms chemical compounds, called *oxides,* with all other elements excepting fluorine and bromine and it will combine with the latter element provided some metal is also a constituent of the compound."—Freer. Much heat is liberated during many of these *oxidations,* i.e., formation of oxides. This indicates that oxygen possesses considerable chemical energy. Substances which undergo oxidation also possess a certain amount of chemical energy in the presence of oxygen, and when they combine with the latter element this energy is converted into heat. Oxygen is ordinarily bivalent.

Experiment I.—Sources of Oxygen.

(*a*) Place a small quantity of mercuric oxide (HgO) in a small test tube. Note its color. Heat bottom of tube strongly and while doing so, introduce a *glowing* splinter of wood. Results? Continue to heat until sides of t.t. show a metallic lustre. Explain. Write the equation for this reaction. When the test tube is set aside and permitted to cool, does the powder in the bottom of the tube regain its original color? Explain. Write the equation for this latter reaction. Is it a reversible reaction?

(*b*) Repeat (*a*) using separately small quantities of MnO_2, CuO, $KClO_3$, and PbO_2.

(*c*) Place a piece of sodium peroxide (Na_2O_2), about the size of a pea, in a test tube half filled with water. Test the evolved gas as in *a* (?). Equation?

$$Hg + O \rightarrow HgO + 30{,}600 \text{ cal.}$$

How many calories of heat would have to be supplied to a gram-molecular weight of HgO to decompose it into Hg and O?

Experiment II.—Laboratory Source of Oxygen.

Thoroughly mix 10 grams of potassium chlorate ($KClO_3$) with exactly 8 grams of MnO_2 (manganese di- or per-oxide); by means of a folded piece of paper introduce the mixture into the large test tube or retort (Fig. 8) which you will find in the drawer; close the tube with a rubber cork fitted with delivery tube; clamp the tube to ring stand at an angle of about 45° so that delivery tube will dip beneath the surface of the water in the pneumatic trough; heat lower end of tube cautiously, and fill six bottles with the gas by displacement of water; place bottles in upright position and cover with wet paper. Observe color, taste and odor of gas as it is

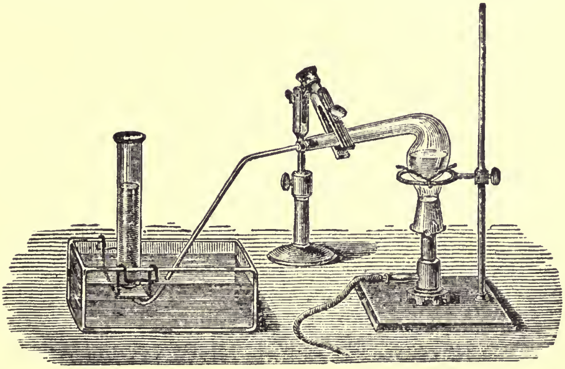

FIG. 8.

evolved; remove delivery tube from pneumatic trough; when tube is cold, add water to contents and allow to soak for several days if necessary to remove mixture; see Exp. VII. Write equation for reaction, remembering that MnO_2 is not altered by the reaction. Proceed with following experiments.

PROPERTIES OF OXYGEN. "KINDLING TEMPERATURE." OXIDATION—OXIDES.

Experiment III.—Oxidation of Carbon.

(*a*) Drop a small piece of charcoal into one of the bottles containing oxygen; immediately recover bottle. Is there any evidence of chemical action? Heat to redness another small piece of charcoal; by means of a pair of forceps, deflagrating spoon or a piece of wire, introduce glowing charcoal into above bottle of gas. Results?

(*b*) Pour a little clear lime-water ($Ca(OH)_2$) into another bottle of the gas; place your hand over mouth of bottle and shake; does the water change in color? Now introduce a piece of glowing charcoal as per above experiment; when charcoal ceases to burn, shake bottle as before. Is there any change in the color of the water? Write equations representing above reactions. If 97,000 calories are liberated by the formation of one gram-molecule of CO_2 from free O and free C, write the "energy equation" for the reaction.

The "*kindling temperature*" of a substance is the temperature to which it must be raised before it will undergo combustion. It is definite for a particular substance but varies greatly for different substances.

Experiment IV.—Oxidation of Phosphorus.

Yellow phosphorus is usually moulded into small cylinders. Place one of these pieces under water and then by means of a knife cut off a piece about the size of a small pea. Never handle P with the hands, as it readily catches fire. Cover the bottom of one of the bottles of gas with water; test water with litmus paper (blue); place phosphorus in a deflagrating spoon (Fig. 9) and ignite it, then lower it into bottle of gas. Results? Test water in bottle with blue litmus paper. Write equations for reaction. Was energy set free by the reaction?

Experiment V.—Oxidation of Sulphur.

By means of a deflagrating spoon, lower a little ignited sulphur into a bottle of gas; the bottom should be covered with water and tested with litmus paper before and after the burning of the sulphur. Results? Was energy liberated? Equations?

Experiment VI.—Oxidation of Iron.

Lower the unwound end of a piece of "picture cord" (iron) into a bottle of the gas for a few seconds. Is there any manifestation of chemical action? Remove the wire and dip it into the burning sulphur in the deflagrating spoon; if the sulphur on the wire is burning, lower wire into bottle (Fig. 10) again. Results? The bottom of the bottle should be covered previously with water to protect it from the molten iron. Write equation. Why was it necessary to burn sulphur on the end of the wire? Was energy set free by the oxidation of the iron?

The greatest diversity of characteristics exists among these *oxides*, which for purposes of convenience may be classed either as *metallic* or *non-metallic* oxides. Many of the elements are capable of forming a series of oxides; nitrogen, for example, forms five different compounds with oxygen. When more than one oxide is formed, the suffix *ous* or *ic* is attached to the name of the metal accordingly as the oxide, relative to the metal, contains a lesser or greater amount of oxygen, i.e., these endings indicate the relative degrees of oxidation which the metals have undergone, thus iron (ferrum) forms two oxides, ferrous oxide (FeO), and ferric oxide (Fe_2O_3); mercury possesses the same property of forming two oxides, mercurous (Hg_2O) and mercuric (HgO) oxides; copper forms cuprous oxide (Cu_2O), and cupric oxide (CuO).

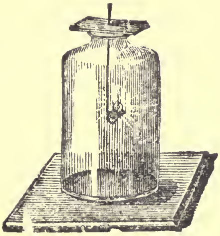

FIG. 9.

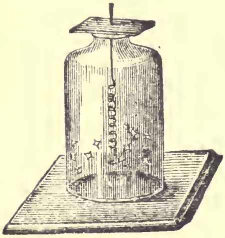

FIG. 10.

Inasmuch as oxygen is ordinarily bivalent, it is obvious that a metal frequently shows a varying valency as represented by its *ous* and *ic* compounds.

In the preceding experiments involving "oxidation," it was readily noted that the reactions were exothermic, i.e., the "heat of formation" of the respective oxides was positive; it follows that the energy (usually heat) necessary to decompose ("heat of decomposition") an oxide is equal to the energy (usually light and heat) liberated during its formation.

This may be made clear by the use of an analogy. As mentioned previously, substances capable of directly combining, possess a definite amount of chemical energy which may be likened unto the potential energy which a stone possesses when it is raised above the ground; when the substances combine, all or portions of the chemical energy of the factors is transformed into say heat and light energy, just as the potential energy of the stone is converted into kinetic energy by permitting the stone to fall; now it will require just as much energy to raise the stone to its original elevated position as was freed during its descent; just so with chemical compounds, the "heat of decomposition" is necessarily equal to the "heat of formation." If combination is attended with the evolution of much energy (heat and light) the oxides will be stable, and *vice versa*.

Although the "heat of combustion" of carbon in oxygen with formation of CO, can not be directly measured, it can be calculated from calorimetric measurements indicated by the following equations:

$$\begin{aligned} & C + 2O \rightarrow CO_2 + 97{,}000 \text{ cal.} \\ \text{and} \quad & CO + O \rightarrow CO_2 + 68{,}000 \text{ cal.} \\ \text{subtracting,} \quad & C + O \rightarrow CO + 29{,}000 \text{ cal.} \end{aligned}$$

Experiment VII.—Catalytic Action of Manganese Dioxide in Exp. II.

This experiment is a continuation of Exp. II. Half fill the test tube with water; heat gently in an endeavor to dissolve contents of tube; be careful to avoid losing any of the solid material; pour the clear supernatant liquid upon a filter; avoid pouring much of the solid matter upon the filter; half fill the tube again with water and heat to boiling; decant the fluid as before upon the filter; repeat above operation four or five times, then pour contents of tube on filter; rinse out tube thoroughly, and wash material upon filter with hot water; spread filter and contents upon wire gauze and heat gently until paper is dry; place paper upon glass plate and scrape black powder into a weighed crucible; fold filter paper and place it in crucible; heat crucible with low flame until contents are perfectly dry, and filter paper has ignited and burned to ash; avoid heating crucible to redness; cool and weigh; ignore weight of ash of filter paper; what is the weight of the black powder? Does this powder resemble MnO_2? Do your results justify the conclusion that WnO_2 was not altered in the reaction? Add a few drops of the filtrate to a cubic centimeter of silver nitrate. Results? Add a few drops of a potassium chlorate solution to a cubic centimeter of silver nitrate. Results? Did the $KClO_3$ undergo a change in Exp. II?

$$\begin{aligned} & 2KClO_3 + 2MnO_2 \rightarrow 2KMnO_4 + 2Cl + \overline{2O} \\ & 2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + \overline{2O} \\ & K_2MnO_4 + 2Cl \rightarrow 2KCl + MnO_2 + \overline{2O} \\ \text{adding,} \quad & 2KClO_3 + 2MnO_2 \rightarrow 2KCl + 2MnO_2 + 6O(3O_2). \end{aligned}$$

A substance which alters the speed of a chemical change apparently by its mere presence and contact, without undergoing any permanent change, is called a *catalytic* agent or simply, a *catalyser*. It may be either a gas, liquid or solid. Pieces of platinum foil are frequently used to catalyse a reaction. The process itself is called *catalysis*.

"To obtain a picture of the way in which a catalyser acts, imagine a wheel-work in which the axles move with great friction, as a result say of the oil having become thick, and which therefore runs down only very slowly. If a little fresh oil be placed on the axles the wheel-work forthwith runs down much more quickly, although the available tension of the spring (which corresponds to the work available from chemical reaction) is in no way altered by the oil. The action of a catalyser may be compared with that of the oil in this respect, and also with respect to the fact that the oil is not used up in acting."—Ostwald.

It should be understood that a catalyser does not *initiate* a reaction; it is not the *cause* of a reaction; it merely increases or diminishes the speed of a given chemical reaction.

Experiment VIII.—Preparation and Properties of Ozone (O_3).

Place two or three pieces of yellow phosphorus, about the size of a "playing" marble, in a bottle; add a sufficient quantity of water to cover bottom of bottle, but not any more than will be necessary to half cover the pieces of phosphorus; four or five drops of a solution of potassium dichromate should be added to the water; cork the bottle. Now prepare a piece of test-paper as follows: dip a strip of filter paper into a starch emulsion to which has been previously added a few drops of a solution of potassium iodide (KI); let the strip of paper "drip" for a few minutes, then suspend it from the cork in the bottle so that paper is within a centimeter of the phosphorus; allow the apparatus to stand for one laboratory period, then examine paper. Note the odor of the gas in the bottle. Results? Equations? The phosphorus should be returned to the supply bottle.

Note.—A good test paper for above experiment is made by dipping a piece of red litmus paper into a solution of KI. When the O_3 acts upon the KI, the iodine is set free and KOH acts upon the red litmus paper turning it blue. Satisfactory results are frequently secured by placing phosphorus in a dry flask which is then closed with a cork.

A quantitative study of the conversion of oxygen (O_2) into ozone (O_3) reveals that 3 volumes of the former are required to form 2 volumes of the latter, and that the reaction is endothermic, i.e., absorbs heat energy.

$$(1)\quad O_2 + O \rightarrow O_3 - 32{,}900 \text{ cal.}$$
$$(2)\quad O_3 \rightarrow O_2 + O + 32{,}900 \text{ cal.}$$

At a temperature of about 275° C. the above reaction (1) is reversed. Ozone is a gas of blue color, odor like dilute chlorine, density 24 ($H_2 = 1$); molecular weight, 47.9; boils at $-119°$ C. Ozone is much more soluble than oxygen in water—100 volumes of water at 12° C. dissolves 50 volumes of ozone under a pressure of one atmosphere. The chemical properties of oxygen and ozone are similar, save that the latter is much more active.

It is evident that oxygen and ozone are identical so far as the kinds of matter of which they are composed is concerned. It seems to be equally as evident that their different properties are due to the fact that they differ in their respective energy contents. When ozone is used as an oxidizer, 32,900 more calories are liberated than when an equal weight of oxygen is used, hence the activity of ozone as an oxidizer. It is to be noted that the heat developed by the passing of ozone into ordinary oxygen is not contained in the ozone, as heat energy but in the form of *chemical* energy.

Ozone and oxygen are *allotropic* modifications of the same element.

Experiment IX.—(Quant.) Determination of, (a) the Density of Oxygen, (b) the Volume of Oxygen Liberated from a Given Weight of Potassium Chlorate, (c) the Weight of the Potassium Chloride Formed.

(*a*) *Note.*—1 gram of $KClO_3$ liberates about 290 $cm.^3$ of O_2.

Place a gas burette, which is connected with a leveling bulb, in a water jacket; suspend a thermometer in the water jacket; raise leveling bulb until water in burette stands at top of capillary tube on upper end of burette. Clean and dry and weigh a hard-glass test tube; record weight; introduce into the tube .12 grm. of $KClO_3$ which has been previously pulverized, and dried in an air bath (100° C.) for one hour. Connect test tube with burette by means of rubber tubing and a piece of capillary glass tubing bent into such form as will permit test tube to be clamped at an angle of about 45°. All joints must be air tight. When making the connections be sure that no water is forced into the glass tubing. Adjust the leveling bulb so that water in it and in burette are at the same level. Read burette and thermometer, and record readings. Holding burner in hand gently warm the test tube; oxygen will be liberated and pass over into the burette. Always keep the water in the leveling bulb about 3 or 4 cm. below the water in the burette. Continue to heat tube until gas ceases to be evolved, then remove burner and allow the apparatus to assume its original temperature, then bring the water in burette and bulb to same level. Read burette, thermometer and barometer, and record readings. From tables in Appendix get vapor tension (a) of water at the temperature of the water jacket. Reduce the volume of oxygen to standard conditions.

$$\frac{\text{Vol.} \times 273 \times (\text{Bar. P.} - \text{a})}{(273 + \text{t}) \times 760} = \text{V.}$$

Remove the test tube; wipe and weigh it; what is the weight of the KCl? The difference between the weight and the original weight of the $KClO_3$ is the weight of the oxygen evolved. Calculate the weight of a $cm.^3$ of oxygen at standard conditions. The weight of a liter? Calculate the weight and volume of oxygen which should have been liberated from the $KClO_3$ on a purely theoretical basis.

Experiment X.—(Quant.) Optional. Determination of the Percentage of Oxygen in the Air.

Note.—The general theory of this experiment is to isolate a given volume of air under known conditions, then bring this volume of air into intimate contact with a substance which will absorb the oxygen, after which the volume of air is measured under the original conditions, and its loss in volume noted.

Use the measuring apparatus assembled for Exp. IX or Hempel burette (Fig. 11). Attach a piece of capillary rubber tubing to the upper end of the gas burette; the tubing should be about 7 cm. long and firmly wired to the burette; place a Mohr pinchcock upon the rubber tubing close to the end of the burette; open pinchcock; raise leveling bulb until water in burette stands at top of capillary tubing, then lower bulb until about 40 cm.^{3} of air have been drawn into burette; close pinchcock; allow gas to stand for five minutes; bring water in burette and bulb to the same level; read thermometer suspended in water jacket, read barometer, read burette, and make a record of readings; now a compound gas pipette (any desirable form, Fig. 12) containing an alkaline solution of pyrogallol,* should be connected with the gas burette by means of a short piece of capillary glass tubing, the pipette should be closed by rubber tubing and a pinchcock; when the pipette and burette are properly connected slightly raise the leveling bulb, then open both pinchcocks and by gradually raising the bulb the air will be forced over into the pipette; raise bulb until water in burette stands at top of rubber tubing on burette; close both pinchcocks; disconnect pipette and burette; shake pipette for 20–25 min.; connect pipette with burette; gradually lower bulb, at the same time open the pinchcocks; continue to lower bulb until all the gas is drawn from pipette

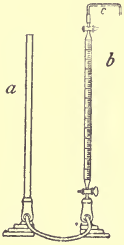

FIG. 11.—Hempel Burette. (Smith and Keller.)

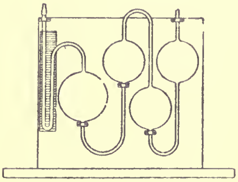

FIG. 12.—Hempel Compound Pipette. (Smith and Keller.)

* The alkaline "pyro" solution is prepared as suggested by Professor Baxter of Harvard, as follows—

One gram of pyrogallol to 4 cm.^{3} of water; 1 gram of KOH to 1 cm.^{3} of water. The solution prepared in above ratio must be mixed out of contact with the air; the pyro solution is first introduced into the pipette after which the KOH solution follows; shake until solutions are thoroughly mixed.

and the "pyro" solution is drawn up to the top of rubber tubing on pipette; close pinchcocks, be sure that both are closed tightly; allow gas in burette to stand for 5 min.; bring water in burette and bulb to same level; read burette, thermometer, barometer and record readings. Repeat the operation until no further decrease in volume occurs. Reduce both the original and final volumes of air to standard conditions. What is the total change in volume? Calculate the percentage of oxygen in the air from your measurements.

A principle of great importance, especially in connection with the measurement of the volume of gases, is incorporated in Dalton's Law of Partial Pressures:

The pressure exerted by a mixture of a gas and a vapor, of two vapors, or of two gases, is equal to the sum of the pressures which each would exert if it alone occupied the whole space afforded to the mixture.

This law is not absolutely exact. It may be stated in another form:

The volumes of two or more gases in a volume of the mixture are proportional to their respective pressures.

Another of Dalton's Laws is:

The pressure exerted by, and the quantity of a vapor which saturates a given space are the same for the same temperature whether this space is filled by a gas or is a vacuum.

PROBLEMS.

1.—How many grams of sulphur will exactly combine with 32 grm. of oxygen to produce SO_2?

2.—What weight of oxygen could be obtained from 10 grm. of $KClO_3$ if the latter contains 10 per cent. of an impurity? Now many liters, if a liter of oxygen weighs 1.428 grm.?

3.—What is the "heat of formation" of SO_2 if 2 grm. of sulphur in burning to sulphur dioxide develops 4440 calories? Write the "energy" equation.

4.—The specific heat of copper is .092. How many calories of heat are liberated when 100 grm. of copper cool from 75° C. to 50° C.?

5.—Is the heat liberated during formation of an oxide, necessarily an accurate measure of the chemical energies (affinity) of the reacting substances? Explain.

6.—Reduce 200 $cm.^3$ of gas at 20° C. and 730 mm. to 0° and 760 mm.

7.—Reduce 45 $cm.^3$ of gas at —20° C. and 770 mm. to 0° and 760 mm.

8.—Reduce 40 $cm.^3$ of gas collected over water at 20° C. and a barometric reading of 730 mm. to 0° C. and 760 mm.

9.—A gas globe when full of air weighed 55.06 grm.; full of water at

20° C. it weighed 309.66 gram. The globe was "exhausted" (air removed) and carefully weighed by means of a counterpoise; it was then filled with a gas at 19.8° C. and 761.4 mm., when it weighed .469 grm. more than when exhausted. What is the weight of a liter of this gas at standard conditions?

10.—What is the molecular weight of the gas used in above experiment?

CHAPTER IX.

HYDROGEN.

Symbol—H. At. Wt., 1.0075.

Hydrogen is a light colorless gas, first described as a form of air (phlogiston) by Cavendish, in 1776, although it had undoubtedly been observed previously by Paracelsus and Boyle. Lavoisier gave the element the name, hydrogene (to produce water). It is univalent.

Experiment I.—Methods for Preparing Hydrogen.

(*a*) Electrolysis of water (H_2O). Recall, or repeat this experiment as previously performed. At which pole was the hydrogen liberated? What test for hydrogen was used?

(*b*) I.—Decomposition of water by means of metals. Wrap a piece of sodium or potassium about the size of a pea in a small piece of filter paper; place it in a small wire cage and dip it under the surface of the water in the pneumatic trough (Fig. 13); hydrogen gas will be evolved, which collect in a test tube by displacement of water; when action has ceased place your thumb over the mouth of tube and hold tube in upright position; place a glowing splinter in the mouth of tube for a second. Results? Bring a lighted match to the mouth of the tube. Results? Does the hydrogen support combustion so far as the glowing match is concerned? When raised to a given temperature does it combine with a component of the air?

$$\underset{\text{Water}}{H_2O} + \underset{\text{Potassium,}}{K} \longrightarrow \underset{\substack{\text{Potassium}\\ \text{Hydroxide,}}}{KOH} + \underset{\text{Hydrogen.}}{\overline{H}}$$

$$H_2O + Na \longrightarrow NaOH + \overline{H}.$$

(*b*) II.—In the above experiment all of the hydrogen of the molecule of water was not displaced by the metal; this may be accomplished by another process. Pulverize and mix thoroughly and quickly about 1 grm. of sodium hydroxide ($NaOH$) and 2 grm. of zinc dust; introduce mixture into a hard glass test tube; heat tube and test for hydrogen gas. Results?

$$Zn + 2NaOH \longrightarrow Zn(ONa)_2 + 2\overline{H}.$$

(*b*) III.—Decomposition of water by magnesium. Shake a gram of magnesium powder into the bottom of a test tube and add 10 $cm.^3$ of water;

add a few cm.^{3} of magnesium chloride (this does not take any part in the reaction, merely dissolving the magnesium oxide which is formed on the surface of the metal). Heat the tube and its contents; test for hydrogen gas. Results? Equation?

(*c*) Displacement of Hydrogen from Acids by Metals.

(*c*) I.—To a small piece of each of the following metals, placed in separate test tubes add 5–10 cm.^{3} of hydrochloric acid, HCl (shelf-reagent); granulated zinc, magnesium (ribbon), iron (filings). Test each tube for the presence of hydrogen. Notice whether the test tubes become warm as the reaction continues. What is the effect of heating the tubes? Record all data. Assume that all of the above metals are bivalent; represent the reactions by "energy equations" using the word "heat" instead of calories. Does the final "system" contain more or less energy than the original one? Why?

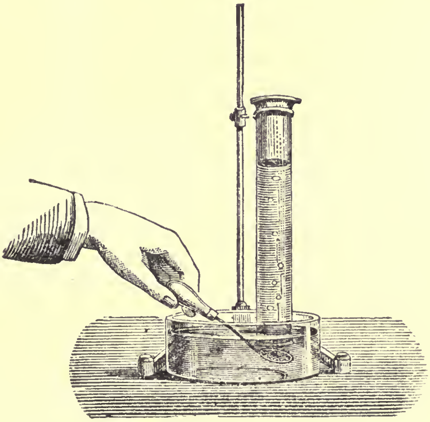

FIG. 13.

(*c*) II.—Repeat (*c*) I, using cold dilute sulphuric acid (H_2SO_4) instead of HCl. This dilute acid may be prepared by pouring 1 volume of concentrated H_2SO_4 (shelf-reagent) *into* 4 volumes of water; allow mixture to cool. Add a few drops of copper sulphate solution to test tubes containing iron and zinc respectively. What is the effect? Similar results are secured by placing a piece of platinum foil or wire in contact with the zinc. This may be verified by the student by using a separate test tube containing zinc and dilute H_2SO_4. After the zinc has dissolved completely, filter the solution which remains; evaporate the filtrate until a thin film appears on the surface when the solution cools. Are crystals deposited? Does it resemble zinc or H_2SO_4? Repeat this process using the iron solution. Write equations as in (*c*) I. Can you explain the action of the platinum or the copper sulphate? Did the platinum lose its identity?

(*c*) III.—Effect of Surface on Speed of Reaction.

Try the action of dilute H_2SO_4 on zinc dust. A small quantity of the latter placed in the bottom of t.t. will be sufficient. Compare results with action of the acid on "granulated" zinc. Explain.

(*c*) IV.—Compare the interaction of acetic acid ($HC_2H_3O_2$) and zinc with foregoing acids and zinc. Repeat above using concentrated H_2SO_4.

The interaction of certain metals with water is identical in principle with the interaction of certain acids and metals; the metallic substance hydrogen, is attached in both cases to a negative element or radical, thus, H.OH, H.Cl, $H_2.SO_4$; the hydrogen (metal) is then displaced by certain other metals, (not all metals, for ex. Au., Ag., Pt.) which possess a greater chemical energy when in contact with the above mentioned negative groups. A reaction then occurs whereby a new system is established which contains less energy than the original one.

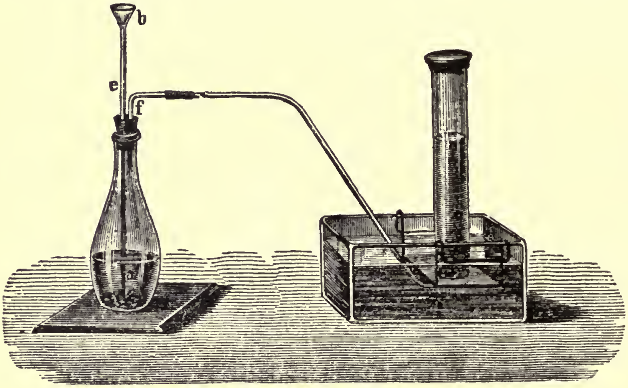

FIG. 14.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2\overline{H}.$$

The "system" represented by the bodies to the *left* of the arrow in the above chemical equation obviously contains more chemical energy than the system represented by those to the *right*, as evidenced by the fact that heat was given out during the reaction.

Experiment II.—Laboratory Source of Hydrogen.

Assemble a gas bottle (generating flask); use the heavy glass flask (Fig. 14) of about 500 $cm.^3$ capacity; fit flask with a rubber cork perforated with two holes; through one of the holes pass a thistle tube; in the other fit a delivery tube with its arms bent at 90°; connect delivery tube of generator with a washing bottle half-filled with concentrated H_2SO_4; washing bottle should be provided with delivery tube which dips beneath surface of water in pneumatic trough. Place enough granulated zinc in the flask to cover the bottom completely; add dilute H_2SO_4 through thistle tube (1 of acid to 4 of H_2O) as needed to secure a rapid evolution of gas; be sure that end of thistle tube dips beneath the liquid in flask. If gas is not evolved rapidly add a few drops of copper sulphate solution through thistle tube. Collect the gas in a test tube by displacement of water until the hydrogen burns quietly in the test tube when a flame is applied to it, then collect several test tubes of the gas and proceed with a study of the properties of hydrogen.

Note.—The test tubes containing the gas must remain inverted with mouths under water. Proceed with Experiments IV and V.

Experiment III.—Properties of Hydrogen.

(*a*) Remove one of the test tubes containing hydrogen from the pneumatic trough and observe whether the gas has any color, odor, etc.

(*b*) Allow one of the test tubes filled with hydrogen to stand mouth upward and uncovered for a minute. Apply a flame. Results? Explain. Is the gas apparently lighter or heavier than air?

(*c*) Place your thumb over the mouth of a tube of gas; hold it vertically, mouth upward; remove the thumb and immediately bring the mouth of a test tube containing air, down over the mouth of the tube of hydrogen, in such a manner as to prevent the gas escaping from the two tubes, but will permit them to "diffuse" into one another; hold them in this position for 1 min.; apply a flame to the mouth of each tube. Results? Explain.

Tabulate the properties of hydrogen as revealed by above experiments.

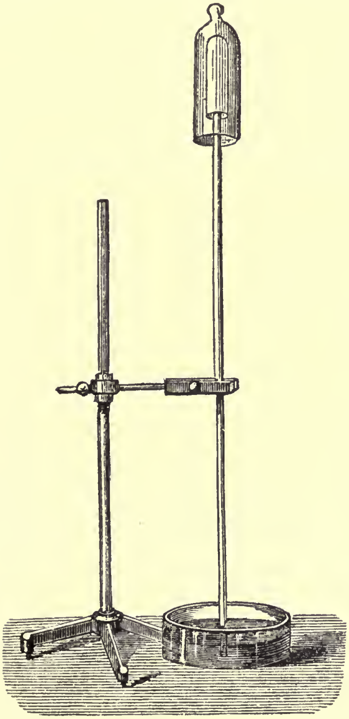

FIG. 15.

Experiment IV.—Effusion of Hydrogen Through a Porous Medium.

As relatively large quantities of hydrogen are required for this experiment (Fig. 15), it can be performed to advantage by the instructor or assistant.

Law of Effusion, of Graham and Bunsen.—*The velocities of effusions of gases are inversely proportional to the square roots of the densities.* Explain on basis of "Kinetic Theory of Gases."

Experiment V.—Synthesis of Water by Burning Hydrogen in Air.

Draw a piece of hard glass tubing out into the form of a fine jet. Attach this jet to the delivery tube of the washing bottle (drying agent in this case); permit jet to dip beneath surface of water in pneumatic trough; fill a test tube with the gas by the usual method; raise jet out of the water; apply flame to test tube of gas; quickly pass the tube over the jet and immediately withdraw it; if gas is pure it burns comparatively slowly so that when tube is passed over jet, the gas issuing from latter is ignited; if gas is impure, i.e., diluted with oxygen, it explodes when flame is applied to test tube. Always light the gas jet by above method. Place over the burning jet a cold dry bottle or let flame impinge upon a cold dry glass plate (Fig 16). Does water form upon the sides of the glass? Is the combination of hydrogen and oxygen to form water an endo- or exothermic reaction? Your reasons? Explain. Equation? When a lamp in a cold room is first lighted moisture appears on inside of chimney. Explain. When bottles of varying sizes are placed over a burning jet, a musical note is frequently emitted; it has been called the "singing flame." Explain.

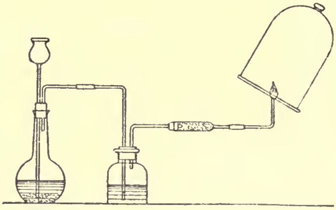

FIG. 16.—(Smith and Keller).

$$H_2 + O \rightarrow H_2O, Aq + 68{,}400 \text{ cals.}$$

Experiment VI.—Hydrogen and Air Form an Explosive Mixture.

The Hydrogen Cannon. Into a small tin vessel closed at one end with a cork, and containing a small opening at the other end, introduce a stream of hydrogen for a few seconds; apply a flame to the small opening after "pointing" cork toward the ceiling. Explain. A mixture of hydrogen and oxygen gases is called "detonating gas." Soap-bubbles filled with this gas will explode when a flame is applied, with a report like a gun.

Experiment VII.—Occlusion of Hydrogen. Catalytic Action of "Spongy Platinum."

Prepare a piece of "platinized asbestos" by dipping a small piece of "sheet asbestos" in a solution of platinic chloride, and then in an ammonium chloride solution; heat asbestos in the hottest portion of the flame of a Bunsen burner or the blast-lamp; finely divided platinum is deposited in the asbestos by this process. When asbestos has cooled slightly hold it by means of forceps or wire so that a current of hydrogen may pass over it. Does the asbestos begin to glow? Is the gas eventually raised to the "kindling temperature"? Repeat, using natural gas or illuminating gas.

"Apparently connected with the catalytic action of platinum is its property of dissolving large quantities of different gases, especially hydrogen." "The hydrogen thereby increases enormously in reactivity . . . . ." "It must not be supposed that the chemical affinity or the chemical potential of the hydrogen is changed; such an assumption, which is certainly very often made, would be a contradiction of the fundamental laws of the theory of energy." "The cause of the changed action of the platinum lies rather in the '*acceleration*' of the reactions of hydrogen and is, therefore, a catalytic action. Gaseous hydrogen reacts so slowly at the ordinary temperature that it appears like an indifferent substance, and from the fact that in the presence of platinum the reaction becomes visible in a short time, while otherwise it would require hours or perhaps years, the view has arisen that there is a change of the chemical potential."—Ostwald. The finely divided platinum, exposing much *surface*, is simply a catalytic agent.

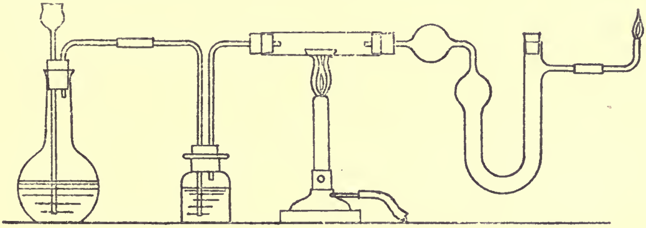

FIG. 17.—(Smith and Keller.)

Experiment VIII.—Reduction of Cupric Oxide—Oxidation of Hydrogen—Synthesis of Water.

Assemble hydrogen generator; connect it with washing bottle (Fig. 17) which should be half filled with H_2SO_4 (conc.), that the hydrogen gas shall be dry after bubbling through it; you will find in the drawer a piece of hard glass tubing 1 cm. in diam. and 18 cm. long; fit into one end a rubber stopper perforated by a single hole; by means of glass tubing connect this end of the tube with the washing bottle—the hard glass tube should be in a nearly horizontal position; the entire system may now be flooded with hydrogen; while waiting for all of the air to be removed from system, spread 1 gram. of cupric oxide (CuO) over the bottom of a small porcelain boat which should then be placed in the middle of the horizontal tube; the portion of the tube beneath the boat should be warmed gently at first, and later, quite strongly. Does moisture condense on cold portions of the tube? Is there any evidence that the CuO has undergone any change?

Remove heat; draw boat out of tube (if water comes in contact with hot tube it will crack); notice the color of the powder. Has metallic copper been deposited? Write equations representing above chemical reactions.

Note.—In above experiment the boat may be dispensed with; place the CuO in the tube. If time permits the reddish-brown powder may be reoxidized by passing a slow current of oxygen over it when heated to redness. Equation?

Experiment IX.—The Nascent State. Nascent Hydrogen.

To 10 cm.^{3} of a dilute solution of potassium permanganate, $KMnO_4$, add an equal volume of dilute sulphuric acid—after shaking divide the solution into two parts. To one portion in a test tube add a little zinc dust; test the evolved gas with a flame. What is the effect of freshly liberated hydrogen, i.e., at instant of liberation or birth, upon the colored solution?

Pass a stream of hydrogen gas through the other portion of the solution. Results? Explain.

Experiment X.—Properties of Hydrogen Dioxide (H_2O_2).

(*a*) From the "side-shelf" reagents procure 5–10 cm.^{3} of H_2O_2. Observe its properties, odor, color, reactive properties toward red and blue litmus paper, etc.

(*b*) Pour a few drops of H_2O_2 upon a piece of "test-paper," or better, upon a little starch paste containing a few drops of a KI solution. Results? Dip a strip of red litmus paper into a dilute solution of potassium iodide (KI); then add two or three drops of H_2O_2 to litmus paper; explain why litmus paper turns blue. Write equations showing nature of above reactions.

(*c*) Heat 5–6 cm.^{3} of H_2O_2 to boiling; test for evolved oxygen; add a pinch of powdered MnO_2 or any powdered metal, preferably the former, to the H_2O_2 in the test tube; test for oxygen. The MnO_2 acts as a catalyser in the reaction:–

$$2H_2O_2 \longrightarrow 2H_2O + \overline{O_2}.$$

(*d*) Test for chromates. Half fill a test tube with H_2O; add 10 to 15 drops of HCl; add a few drops of potassium dichromate solution to impart a brick red color to solution in test tube; add a layer of ether 2 cm. thick; add two or three drops of H_2O_2; shake. Is the ether colored blue? This blue color is supposed to be due to presence of perchromic acid ($H_2Cr_2O_8$), probably formed as indicated by following equations:—

$$K_2Cr_2O_7 + 2HCl \longrightarrow H_2Cr_2O_7 + 2KCl\ (?)$$
$$H_2Cr_2O_7 + H_2O_2 \longrightarrow H_2Cr_2O_8 + H_2O.$$

A chromate made strongly acid with HCl may be used instead of the $K_2Cr_2O_7$ solution. The H_2O_2 acts as an oxidizer.

(*e*) H_2O_2 as a reducing agent and a bleacher. To a few cm.^{3} of a potassium permanganate add an equal volume of H_2SO_4; now add sufficient H_2O_2 to decolorize the solution.

$$KMnO_4 + H_2SO_4 \rightarrow HMnO_4 + KHSO_4.$$
$$2HMnO_4 + 2H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + 8H_2O + \overline{5O_2}.$$

(*f*) Bleaching with H_2O_2, a process of oxidation. To a few drops of indigo solution add 5 cm.^{3} of H_2O, then add 4 or 5 cm.^{3} of H_2O_2; heat. Results?

$$C_{16}H_{10}N_2O_2 + 2H_2O_2 \rightarrow 2C_8H_5NO_2 + 2H_2O.$$

Experiment XI.—Preparation of Hydrogen Dioxide.

Half fill a test tube with H_2O; add about 20 drops of dilute HCl and a sufficient quantity of a potassium dichromate ($K_2Cr_2O_7$) to impart a brick-red color to the solution; add ether until there is a layer 2 cm. thick; make a thick paste of BaO_2 and H_2O; add this paste to the contents of the t.t.; shake and observe the color of the layer of ether. Compare results with Exp. X (*d*). Write the equation for the interaction of BaO_2 and HCl. Another method for the preparation of H_2O_2 is represented by following equation: Decant the solution which is formed as the result of the reaction,

$$BaO_2 + H_2SO_4 \text{ dil.} \rightarrow Ba_2SO_4 + H_2O_2,$$

into a clean test tube; add ether, and a few drops of a dilute solution of potassium dichromate.

$$H_2 + O_2 \rightarrow H_2O_2, Aq + 45{,}300 \text{ cal.}$$
$$H_2O_2 \rightarrow H_2O + O + 23{,}100 \text{ cal.}$$
$$H_2 + O \rightarrow H_2O, Aq + 68{,}400 \text{ cal.}$$

Experiment XII.—(Quant.) Optional. Synthesis of Water.

Recall or repeat Exp. "Combining Volumes, "under head of "Quantitative Relationships."

Experiment XIII.—(Quant.) Hydrogen Equivalent of Zinc, or a Determination of the Volume of Hydrogen Evolved from Sulphuric Acid by a Given Weight of Zinc.

Assemble gas measuring apparatus described in Exp. X. under "Oxygen." Raise leveling bulb until water in gas burette stands at top of capillary on burette; clean and dry a 150 cm.^{3} bottle which has a small test tube fused into the bottom (this test tube need not be fused to bottle); fit to bottle a rubber cork perforated with one hole; by means of a short piece of capillary glass tubing connect bottle with top of burette. Clean and dry a piece of pure sheet zinc; weigh a piece of this zinc with great accuracy; the piece must not weigh more than .13 grm. if the capacity of burette is 50 cm.^{3}; carefully wrap a piece of platinum wire around the zinc (the platinum acts as a catalyser); the piece of zinc should now be dropped into the bottle; 25 c.m^3 of pure H_2SO_4 (1 of acid to 4 of H_2O) is carefully placed in the test tube in the bottle by means of a pipette; the cork is forced into place and air-tight connections are made with the burette. It is well to place bottle in a water bath; allow the apparatus as assembled to stand for five minutes; level; take temperatures of water bath and water jacket, read burette, read barometer; record all readings; turn bottle until acid is poured out of t.t. upon zinc; gradually lower the leveling bulb as the gas is evolved; after all the zinc has been exhausted and gas is no longer evolved, allow the apparatns to stand for a few minutes; bring the water bath and the water jacket to their respective initial temperatures; bring water in burette and bulb to same level; read burette; reduce volume of gas to 0° C. and 760 mm. If the weight of 1 cm.^{3} of hydrogen at 0° C. and 760 mm. is .00009 grm. how many grams of hydrogen will be evolved by 32.7 grams of zinc?

Calculate both the weight, and the volume (at standard conditions) of hydrogen which should have been evolved from the acid by the weight of zinc used. Compare experimental data with calculated.

Note.—A few drops of $PtCl_4$ added to the acid could have been substituted for the platinum wire. $CuSO_4$ is also frequently used, but a correction factor is necessary owing to the following indicated reaction—

$$Cu\,SO_4 + Zn \rightarrow Cu + ZnSO_4.$$

OUTLINE OF HYDROGEN.

I.—History of Hydrogen.
  (*a*) Discovery—when and by whom?
  (*b*) Derivation of name. (Gr. *hudor* (water), and *geinomai* (I produce).)
  (*c*) Historical in connection with (*a*) and (*b*).

II.—Occurrence or Distribution.

III.—Methods of Preparation.

IV.—Physical Properties.

Colorless,
Odorless,
Tasteless,
Wt. of 1l., .09 grm.
Density (O = 16), 1.008.
Density (Air = 1), .0696.
Sp. Ht. (gas at const. pres.) 3.409.
Sol'ty in Aq., 1.82 vols. in 100 (20° C.).
Diffuses rapidly.
Melting point, —256° to —257° C.
Boiling point, —252° to —253° C.
Crit. Temp., —238° to —240° C.

Note.—K. Olszewski, in an attempt to liquefy helium, cooled the gas to —259° C. under 180 atmospheres' pressure, by the aid of solid hydrogen; the pressure was suddenly reduced to that of the atmosphere which should give a degree of cold as calculated by Laplace and Poisson's formula, equal to —271.3° C. Helium did not liquefy. This is the lowest temperature recorded to date.

V.—Chemical Properties.—Hydrogen, in the majority of its chemical relationships, displays the characteristics of a metal, and because of this it is usually regarded as a gaseous metal* at ordinary temperatures.

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* NOTE.—Since hydrogen does not form a base with oxygen and because its combinations with many of the non-metals are acids and not salts, it does not come within the ordinary definition of a metal.

It is practically diametrically opposed to oxygen. It is liberated at the negative electrode by the electric current during electrolysis; it is displaced from many of its compounds by metals, i.e., hydrogen functions as a metal; sodium and potassium absorb hydrogen when heated from 250° to 400° C., forming alloys (Na_2H and K_2H—Richter); similarly the compound PdH_2 conducts itself like an alloy of two metals; according to Graham the specific gravity of the condensed hydrogen in these compounds is found to be .62, which makes it somewhat heavier than the metal lithium. Hydrogen combines energetically with oxygen, fluorine, chlorine and the metal lithium; however, it unites directly with but few of the elementary substances. Its "affinity" for oxygen and chlorine under certain conditions is such that it will displace the elements with which they are united. When oxygen is taken away from a compound by hydrogen, the latter is said to be *oxidized* and the compound *reduced.*

The thermochemical deportment of hydrogen and oxygen in the formation of the two compounds, H_2O and H_2O_2, is interesting.

$H_2 + O \longrightarrow H_2O$ (18 grm. at 20° C.) + 68,360 cals.
$(H_2 + O)$ 3 vols. $\longrightarrow H_2O$ (2 vols. steam) + 193 cals.
H_2O (steam, 100° C.) $\longrightarrow H_2O$ (water, 100° C.) + 9,666 cals.
H_2O (water, 100° C.) $\longrightarrow H_2O$ (water, 20° C.) + 1,440 cals.
193 cals. + 9,666 cals. + 1,440 cals. = 11,299 cals.
68,360 cals. —11,299 cals. = 57,061 cals.

The approximate *thermal equivalent* of the *chemical energy* of a mixture of 2 grm. of hydrogen and 16 grm. of oxygen is 57,061 cals.

The "Law of Hess" is suggested by the thermo-chemical conduct of hydrogen dioxide:

$$\begin{array}{rl} & (1)\ H_2 + O_2 \longrightarrow H_2O_2Aq + 45{,}300 \text{ cal.} \\ \text{and} & (2)\ H_2O_2 \longrightarrow H_2O + O + 23{,}100 \text{ cal.} \\ \hline \text{adding} & (3)\ H_2 + O \longrightarrow H_2O + 68{,}400 \text{ cal.} \end{array}$$

No matter how many stages there are to a given reaction, if the initial and final states are the same in each case, the heat of the reaction will be constant.

On inspecting equation (2) it is obvious that H_2O_2 is an active oxidizer, as it liberates 23,100 cal. more than when the same amount of free oxygen is used under similar conditions. This serves to explain its activity as an oxidizer in foregoing experiments. Which is the more active oxidizer O_3 or H_2O_2? Hint—compare energy equations.

Compounds of Hydrogen.—To be studied as work progresses.

Uses of Hydrogen.—Oxy-hydrogen blowpipe, calcium light, etc.

Miscellaneous Topics.—Principles, theories, definitions, etc.

Note.—In the future the student will make a brief written "resume" of the study of each element. It should embrace the various heads, under which data is to be tabulated, as suggested above in the "Outline of Hydrogen."

PROBLEMS.

1.—What is the weight of 100 $cm.^3$ of hydrogen at 20° C. and 760 mm.?

2.—How many grams of zinc will be required to liberate 10 grams of hydrogen from sulphuric acid?

3.—What is the weight of a liter of hydrogen measured over water at 20° C. and 777.36 mm.?

4.—How many liters of hydrogen can be obtained from 100 $cm.^3$ of sulphuric acid (density, 1.84)?

5.—How much zinc and sulphuric acid will be required (theoretically) to liberate 1 liter of hydrogen?

6.—A liter of oxygen weighs as much as what number of liters of hydrogen?

7.—Two grams of hydrogen are equivalent to how many liters of the gas at standard conditions?

8.—What are the valences of the elements in the following: HCl, H_2O, Na_2O, NH_3, KCl, LiH, H_2S, CO_2, FeO, Fe_2O_3?

9.—If a liter of hydrogen weighs .09 grm. what is the weight of a liter Of O_2? Of CO_2? Of N_2? Of Cl_2?

10.—What are the relative rates of effusion of hydrogen, oxygen and carbon dioxide?

11.—Why is the oxygen admitted through the inner tube of the oxy-hydrogen blowpipe? Note: The temperature of the hydrogen flame in air is about 2000° C.; in oxygen it is about 2500° C. It can not surpass this latter temperature as it is the temperature at which steam is resolved into its elements.

12.—What are the formulæ of cuprous and cupric oxides? Of ferrous and ferric oxides? Of ferrous and ferric chlorides?

13.—Is the process of *oxidation* accompanied by the process of *reduction?* Illustrate by equations and interpret.

14.—Is *occlusion* a chemical or physical action? State your reasons.

15.—Mention a reaction in which the speed was altered by *surface effects.*

CHAPTER X.

WATER.

In all investigations, the product of the interaction of two volumes of hydrogen and one volume of oxygen, has been proven to be identical with the substance which is known as **water.** It is one of the most abundant and universally distributed of all chemical compounds. It is essential to life. Its properties are remarkable and diversified.

In 1781, Cavendish confirmed the formation of water by the combustion of hydrogen. Prior to his work, water was thought to be an elementary substance. Lavoisier determined its quantitative composition in 1783. In 1805, Gay-Lussac showed that it was produced by the union of two volumes of hydrogen with one volume of oxygen. Water was first decomposed by electricity in 1800 by Nicholson and Carlisle. Davy confirmed and extended the work of these men, aside from initiating many brilliant experiments. The names of the men who were connected with the study of water are, Cavendish, Priestly, Lavoisier, Humbolt, Gay-Lussac, Nicholson and Carlisle, Berzelius, Davy, Dumas, Dulong, Stas, and Morley.

Experiment I.—Composition of Water.

(*a*) Synthesis of water. Recall or repeat the various experiments involving the "synthesis of water."

$$2H_2 \text{ (two vols.)} + O_2 \text{ (one vol.)} \longrightarrow 2H_2O \text{ (two vols.)}$$

Recall "Law of Combining Volumes." State it.

(*b*) Analysis of water.

1. By electrolysis.
2. By action of metals.

$$4H_2O \text{ (steam)} + 3\,Fe \text{ (hot)} \rightleftarrows Fe_3O_4 + 4H_2 \text{ (Fig. 18).}$$

At a high temperature, steam oxidizes those elements which readily combine with oxygen. Recall the respective oxidizing activities of O_2, O_3 and H_2O_2. Compare their respective energy equations with that of steam when each is acting as an oxidizing agent.

Experiment II.—Physical Properties.

(*a*) Quant.) Density. Clean and dry a 50 $cm.^3$ Erlenmeyer flask; weigh it. By means of a burette or a pipette introduce into the flask 15 $cm.^3$ of distilled H_2O which has a temperature of about 20° C.; weigh flask and contents as rapidly as possible to prevent loss by evaporation. Calculate the approximate density of H_2O under the existing conditions. See "Table of Density" in Appendix.

Note.—Burettes filled with distilled H_2O may be placed in readily accessible places in the laboratory.

(*b*) Freezing point. Fill a beaker with a mixture of clean ice and water; the ice should be broken into small pieces. Suspend a thermometer in the mixture for 5 or 10 min.; the mixture should be stirred. Tap the thermometer with finger and read. Record reading.

(*c*) Boiling point. Measure 20–25 $cm.^3$ of distilled H_2O into a clean Erlenmeyer flask; suspend a thermometer in the flask so that its bulb is about 2 or 3 cm. above surface of H_2O; heat flask and contents until there is a rapid evolution of steam; tap thermometer, and read. Record reading. Suspend thermometer so that bulb dips into water but does not touch bottom of flask. Repeat above. Record reading. Read the barometer. (Instructions.) Record reading.

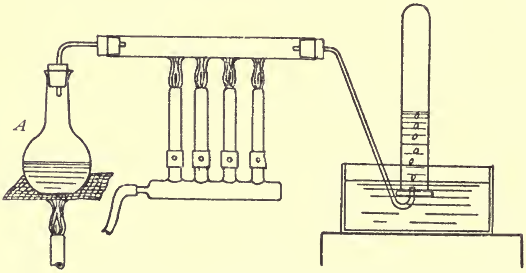

FIG. 18.—(Smith and Keller.)

Experiment III.—Purity of Water.

Place a few drops of distilled water upon a clean "watch glass" and evaporate to dryness upon a steam bath. Is there a stain or residue on glass? Repeat above using ordinary water, for example, "drinking water." Compare results with above. If the impurities of the water are very volatile will this method enable you to detect them? Why?

The preparation of "absolutely" pure water is an impossibility, as the material of any vessel is soluble in a greater or lesser degree.

Experiment IV.—"Temperature-Density" Graph of Water.

By referring to the table in the Appendix, plot on "coordinate paper" the "temperature-density" graph of water. Use the axis of ordinates for the scale of density and the axis of abscissas for temperature-scale. (Instructions.)

Does the comparatively abrupt change in the direction of graph suggest the introduction of a new "factor" in the phenomena which graph is supposed to represent? May this change in direction merely represent that a factor or a group of factors has suddenly become dominant?

Experiment V.—Purification of Water.

I.—Chemical Methods.
II.—Mechanical Methods.
  Decanting.
  Filtering.
  Boiling.
  Distillation.

(*a*) Distillation of a solution of copper sulphate. Assemble a distilling apparatus, composed of a distilling flask, Liebig condenser (Fig. 19) and a receiver, or use a retort and a receiving flask. (Instructions.) Test solution with litmus paper; test distillate with litmus paper; compare results. How does color of distillate compare with color of original solution?

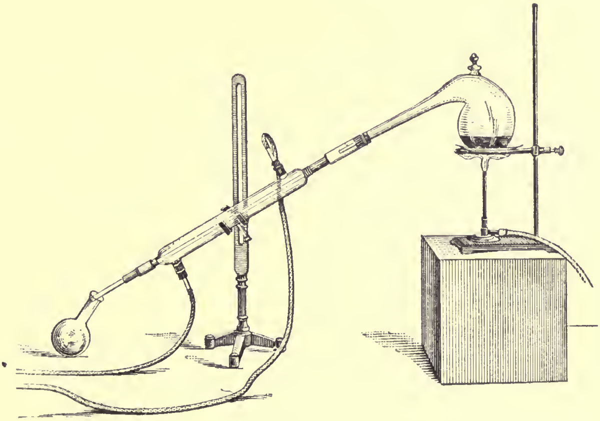

Fig. 19.

(*b*) Distillation of a solution of ammonium hydroxide. Proceed as in (*a*) Results? Explain.

(*c*) Distillation of a solution of alcohol. Proceed as in (*a*), but test inflammability of solution and distillate by means of a lighted match. Explain. Recall "Law of Partial Pressures."

Note.—Boiling-tubes prevent "bumping" of solutions undergoing ebullition.

Experiment VI.—Hydrolysis.

To a small quantity of bismuth chloride, Bi Cl_3, or antimony chloride, $SbCl_3$, add 5 $cm.^3$ of water; the white precipitate is essentially bismuth oxychloride, BiOCl. To the precipitate add a few drops of concentrated hydrochloric acid, then warm tube; by repeating this process dissolve the precipitate in a minimum quantity of acid. The tube contains a solution of $SbCl_3$. To a test tube nearly full of water add a few drops of the solution. Explain the formation of the white precipitate. Write equations for the three reactions.

Experiment VII.—Chemical Union of Water with Oxides.

(*a*) Combination with a metallic oxide. Place a small quantity of quick lime (CaO) or barium oxide (BaO) in a test tube; add 5–10 cm.^{3} of H_2O which has been previously tested with litmus paper; shake vigorously; let contents settle; decant clear liquid into another test tube and test liquid with litmus paper. Results? Equation? Substances like the above which turn red litmus blue are called "*bases.*"

(*b*) Combination with a non-metallic oxide. Recall the action of P_2O_5 and SO_2 on the *moist* litmus paper. Record results. Substances formed by the union of non-metallic oxides and water and which turn blue litmus red, are called "*acids.*"

Experiment VIII.—Water of Hydration (Crystallization).

(*a*) Place a small crystal of copper sulphate ($CuSO_4.5H_2O$) in a test tube; heat gently until a white powder remains. Is there evidence that water has been liberated during the above process? Add a drop or two of water to the powder when tube is cool. Effect? Add water and boil, dissolving the powder in the least possible quantity of water; set tube aside for several days; do crystals form?

(*b*) Using crystals of gypsum, potassium dichromate, barium chloride and potassium nitrate, ascertain whether water is present in each crystal.

Note.—Some crystals contain "mechanically inclosed" water; when such crystals are heated they fly to pieces explosively: they are said to *decrepitate.* Did any of the above crystals decrepitate?

Do all crystals contain *water of hydration?* Reasons for your answer?

A salt containing water of hydration is spoken of as a *hydrated* salt; when the water has been removed it is known as an *anhydrous* or *dehydrated* salt.

Experiment IX.—Vapor Tension of Substances. Efflorescence and Deliquescence.

(*a*) Examine a small clear crystal of sodium sulphate, $Na_2SO_4.10\ H_2O$; place it on a clean watch glass and set it in closet; after several days examine. Explain. Equation? The substance is said to be *efflorescent.*

(*b*) Place a piece of dehydrated calcium chloride, $CaCl_2$ in a beaker. Repeat (*a*). Explain. Equations? The substance is said to be *deliquescent.*

(*c*) Introduce 10 cm.^{3} of concentrated sulphuric acid into a dry test tube; mark its height by means of a piece of label or an ink mark; allow it to stand for a week. Explain.

Experiment X.—(Quant.) Determination of Water of Crystallization.

Weigh accurately a clean dry crucible and cover. Record weight. Introduce into crucible about 2 grm. of powdered copper sulphate crystals; place cover on crucible and weigh accurately. Record weight. Place covered crucible on a pipe-stem triangle and heat gently for about 25 min. or until quite certain that the blue color has completely disappeared; cool in desiccator, then weigh. Record weight. Heat again for 5–10 min. and weigh. Repeat until weight becomes constant. Calculate the percentage of water of crystallization of the crystals.

Note.—In applying heat to the crucible, the tip of the flame may barely touch the bottom of the crucible.

Physical Properties of Water.

Tasteless.
Odorless.
Colorless (in thin layers).
Density (1 cm.^{3} at 4° C.), 1 grm.
Sp. Ht. (Solid state), .50.
Sp. Ht. (Liquid), 1.00
Sp. Ht. (Gas), .477.
Ht. of Fusion, 80 cals.
Ht. of Vaporization, 536.7 cals.
Melting point, 0° C. 760 mm.
Boiling point, 100° C. 760 mm.
Crit. temp., 370° C. (Highest critical temperature known.)

The specific heat of water is remarkably high. More heat is required to raise the temperature of a given weight of it one degree than is required for any other substance except hydrogen.

Chemical Properties.—Water is one of the most stable of all substances, i.e., it is not easily decomposed as regarded from the standpoint of energy, yet like other chemical compounds it is broken up into its elements by heat. "Sainte-Claire Deville was the first to carefully investigate and explain the decomposition of water by pouring molten platinum (1770° C.) into it." "He proved that the *dissociation*—a reversible decomposition—did not take place suddenly, but gradually; that it advanced regularly with increasing temperature, and was limited by an opposing combination-tendency on the part of the components."—Richter.

$$2H_2O \rightleftarrows 2\overline{H}_2 + \overline{O}_2.$$

The decomposition is appreciably initiated at 1000° C. and is about half complete at 2500° C. The percentage of dissociation increases with increase of temperature.

Water bears evidence of being slightly dissociated when in the liquid condition as well as when in the gaseous state. Electrical conductivity and certain chemical reactions indicate the truth of the following equation:

$$H_2O \rightleftarrows H^+ + OH'.$$

This will be discussed more fully under the subject of "The Modern Theory of Solution." Water is usually referred to as a perfectly neutral substance, but this is far from agreeing with experimental facts. Owing largely to the products of dissociation, water manifests definite chemical properties under definite conditions.

Another interesting property of water is one which is thought to be closely related to the varying density of water with change of temperature. In virtue of this property the molecules of water are supposed to *associate*, that is, a number of molecules combine and form a "molecular-complex." This phenomenon is known as the *polymerization* of water. "Surface tension" and "depression of the freezing point" experiments support this view. Raoult and others hold that at temperatures near the freezing point, a relatively large quantity of the water possesses the molecular formula, H_8O_4 or $(H_2O)_4$. Increase in temperature causes a breaking up of these molecular-complexes, and vice versa. The change in density of water with change of temperature is explained in general as follows:

The H_8O_4 molecules occupy more space than $4H_2O$; polymerization increases as temperature is lowered; water contracts when the temperature falls; two factors must then be considered. Water expands when cooled below 4° C. because the effects of polymerization overbalance the effects due to contraction as the result of lowering the temperature. When the temperature is increased to 4° C., the water should expand normally, and probably does, but the molecular-complexes tend to split up which *per se* causes a shrinkage in volume; at 4° C. the effects of the two factors balance each other, hence the maximum density at this temperature. If the temperature is raised above 4° C., then the expansion-effects due to increase of temperature are greater than the contraction-effects due to a breaking down of the associated molecules. Above 4° C. the effect of cubical expansion due to increased temperature is dominant; below 4° C., expansion-effects due to increased polymerization are dominant.

It was said in the beginning of this chapter that water in its chemical relations presents some very remarkable features; one of the most marked is, that although it is an indifferent oxide (hydrogen oxide), it possesses a group of combining tendencies which extend over a wider range than those of any other chemical compound. It combines directly with many compound substances, but with few elements—chlorine and bromine being perhaps the only elementary substances. Gases are dissolved by water to a relatively slight extent, but it can not be affirmed positively that they enter into a chemical combination. The most common of its chemical reactions is the formation of a class of compounds known as *hydrates*, which exist in the solid form only, undergoing decomposition when placed in solution, Ex.s. $CuSO_4.5H_2O$, $Na_2SO_4.10\ H_2O$. They show a definite composition and frequently much heat is developed during their formation, thus $(Na_2CO_3,\ 10\ H_2O)$, equals 8800 cal. Water also reacts with some substances in a manner which is very similar to metathesis—to say that the products of dissociated water, rather than the water *per se*, interacts with substances to produce double decomposition, is a statement more nearly in accord with facts. This kind of a reaction is known as **hydrolysis.** The mechanism of the interaction may be interpreted more readily by the aid of an equation.

$$H_2O \rightleftarrows H^+ + OH$$
$$Bi^{+++} + 3Cl' + 2H^+ + 2OH' \rightleftarrows Bi\,\underline{(OH_2)Cl} + 2H^{+\prime} + 2Cl'$$
$$Bi(OH)_2Cl \rightleftarrows \underline{BiOCL} + H_2O.$$

If the product of hydrolysis is soluble there is usually little or no visible evidence of the interaction; if the product is insoluble a precipitate forms. As the work advances the phenomenon of hydrolysis will be more thorough discussed. A familiar example of the direct combination of water and metallic and non-metallic oxides is the slaking of quicklime which may be represented as follows:

$$CaO + H_2O \longrightarrow Ca(OH)_2 \text{ (Calcium Hydroxide),}$$
again, $$SO_2 + H_2O \longrightarrow H_2SO_3 \text{ (Sulphurous Acid).}$$

The product of the first reaction belongs to a group of substances known as *bases;* the latter product, to a group whose generic name is *acids.* The chemical properties of these two groups, acids and bases, are very different; an aqueous solution of the former turns red litmus paper blue, while in the case of the acids, blue litmus paper is turned to a red color.

However, of all the various properties of water, perhaps none are of more importance to the chemist than its *solvent* properties. The question as to whether the effecting of a solution is a chemical or physical process has not been satisfactorily answered. This question will be discussed more fully in the next chapter.

In addition to its enumerated uses, it should be remembered that water is the standard of many physical measurements.

CHAPTER XI.

SOLUTIONS.

We have observed that many gases, liquids and solids when placed in water disappear and form homogeneous systems which are known as solutions. The operation of preparing a solution is called "dissolving" or "putting into solution." The substance dissolved is known as the *solute* and the material in which the solute is dissolved, the *solvent.* These two terms are unfortunate inasmuch as they do not suggest the mutual interaction of solute and solvent during the process of dissolving. *All substances are soluble in a degree,—the solubility depending upon the relative strength of the affinities of the substance for itself and for the solvent.* If the affinity of solvent and solute is greater than the affinity of substance for self, then the solubility will be correspondingly great. The degree of solubility is usually expressed by the terms *insoluble, slightly soluble, soluble,* and *very soluble.* When the solution contains a relatively large quantity of the solute it is said to be a *concentrated* solution; if a relatively small quantity, a *dilute* solution.

"Since matter in every state can be mixed with other matter, irrespective of its state, it is obvious that many different kinds of solutions are possible." Jones (H. C.) gives the following list:

I. Solution of a solid in a solid.
II. Solution of a solid in a liquid.
III. Solution of a solid in a gas.
IV. Solution of a liquid in a solid.
V. Solution of a liquid in a liquid.
VI. Solution of a liquid in a gas.
VII. Solution of a gas in a solid.
VIII. Solution of a gas in a liquid.
IX. Solution of a gas in a gas.

Among the properties of solutions may be noted—color, odor, taste, density, expansibility, compressibility, surface tension, viscosity, vapor tension, osmotic pressure, refractive index, definite boiling and freezing points, etc.

SOLUBILITY OF SOLIDS.

Experiment I.—Characteristics of a Solution.

Powder separately a few small crystals of alum, and potassium dichromate; dissolve each in the least possible quantity of water—the test tubes should be shaken and warmed repeatedly to aid in the process. Are the solutions clear? Transparent? Homogeneous? Pour the solutions into separate crystallizing dishes, or set the tubes aside to cool.

Do crystals form? If so, decant the liquid and examine crystals. Are they similar to the original crystals?

A *solution* is ordinarily defined as *a clear transparent homogeneous mixture*, the *components of which can not be separated by a purely mechanical process.* "Colloidal" or "pseudo-solutions"—see Ostwald's "Principles of Chemistry." p 24

Experiment II.—Surface and Diffusion Phenomena. Solution Tension.

Half fill a test tube with water; drop one small crystal of potassium permanganate into the water; set tube where it will not be shaken, yet can be easily observed; as you continue your experimenting, notice the color of the solution at short intervals of time. Record observations. Was a relatively long period of time required for the dissolving of the crystals? Postulating that the salt is quite soluble in water at a given temperature, what factors determine largely the speed of the dissolving process? To what two mechanical processes do we resort usually in an endeavor to hasten solution? Did any phenomena occur during the dissolving of the solid which would suggest any of the properties possessed by liquids or gases? Enumerate them.

The process of solution receives a partial explanation, at least, when the accompanying phenomena are interpreted in terms of the kinetic-molecular hypothesis. When a soluble crystalline substance is introduced into the solvent, it is thought that the molecules of which the solute is composed are detached and enter the solvent. By the process of *diffusion* these detached particles move away from the *surface* of the solute, and are scattered throughout the solvent. After a time some of these particles, which move in every direction, will again come into contact with the solid solute and attach themselves to it. If the rate at which the molecules press into solution is greater than that with which they return to the solute, it is evident that the solute will eventually be wholly dissolved. If a sufficient quantity of the solid substance has been placed in the solvent the dissolving process will continue until the speeds of the two opposing actions are identical. When this occurs the solution is said to be saturated. The solid solute is then in equilibrium with the dissolved portion,

$$KMnO_4 \text{ (Solid)} \rightleftarrows KMnO_4 \text{ (Dissolved)}.$$

If this equilibrium is disturbed by varying the concentration of the solution, the speeds of the opposing actions will be altered until equilibrium is again established, either by the dissolving of more of the solute if the concentration is decreased, say by diluting the solution; or by the deposition of a portion of the solute if the concentration is increased by any cause whatever—say the removal of a portion of the solvent. The experimenter is never assured of the existence of an equilibrium unless a portion of the solute (solid) is in contact with the solution. Powdering the solute and shaking the mixture hastens the process of solution. Why?

This tendency of the molecules of a substance when placed in a solvent, to leave the solid and pass into solution is referred to as *solution tension* because of its evident analogy to the vapor tension of liquids, in virtue of which liquids tend to assume the gaseous condition. The analogy is continued: There is equilibrium when the vapor tension of a liquid is balanced by the gaseous pressure of the vapor above it; likewise there is a dynamic equilibrium in a saturated (concentrated) solution between the dissolved and undissolved portions of the solute; the force (energy) in virtue of which the molecules tend to pass into solution is usually spoken of (mentioned previously) as the *solution tension* of the solute; the force in equilibrium with the solution tension, and which is considered as the analogue of the gaseous pressure of the vapor above a liquid, is known as *osmotic pressure.* In this pressure we recognize the cause of the diffusion of substances in solution. It has been discovered that the molecules of a dissolved substance like sugar, exert a pressure on the solvent identical with the pressure which they would exert on the sides of a vessel of the same volume as that of a solution, if they were in the gaseous state. This pressure is given the name *osmotic pressure* because it is only by taking advantage of the phenomenon of *osmosis* (which provides for the elimination of "surface pressures") that it can be rendered apparent and directly measured.

The correlation of much experimental data which will be discussed as the work proceeds, has given rise to what is known as the "physical theory" of dilute solutions. It may be stated as follows: "The molecules of the dissolved substance pervade the solvent without being influenced thereby, and possess the same properties as they would possess did they alone, in the state of gas occupy the volume filled by the solution."—Bloxam. It seems that there is more likelihood of the dissolved substance being in a condition comparable to a gas than to either a liquid or a solid. It is obvious that it can not be in a state of aggregation comparable to a solid.

Hulett (J. Amer. Chem. Soc., 27, 49, 1905) recently presented an interesting article on the importance of the *state* of the solid from which the solution is made. The real subject of the article, however, is an explanation of the greater speed of solution and greater solubility of very small particles of a solid as "based on the following considerations: The boundary between a solid and a liquid is the seat of a certain amount of energy due to the surface-energy of the liquid; if this surface is increased by powdering the solid, the total surface-energy is correspondingly increased. Further, it is a generally observed fact that the form of a substance which has the greater free energy is the more soluble, has the greater vapor-pressure, and is the least stable form, e.g., allotropic modifications of substances have different solubilities, and the unstable form is always the more soluble. This phenomenon is hardly analogous to the well known behavior of liquid drops of different sizes. Small drops in the vicinity of large ones grow small and disappear, while the larger ones grow larger, and the reason is quite clear. It is known that the curved surface of a liquid has a greater vapor-pressure than a plane or less curved surface; therefore, a distillation takes place. The similarity between the vapor-pressure of liquids and the solution-pressure of solids has suggested to some the analogy between the facts just mentioned and the behavior of solid particles of different sizes in contact with the solution. But we can not assume that the surface of the particles of a powder is curved, or, if that is granted, we do not know that a curved surface of a solid or a sharp edge has a greater solution-pressure than a plane surface of the same substance.

"Hulett found that a solution of gypsum saturated at 25°, containing 2.080 grm. $CaSO_4$ per liter will increase its concentration rapidly to a maximum when shaken with powdered gypsum and then will decrease to the original value again. In one experiment the content of gypsum reached 2.542 grm. $CaSO_4$ in a liter in a minute. The fine powder used for this purpose was found, after the concentration had reached its original point, to have increased in size of its grain. The smallest particles thus go into solution, produce the supersaturation and are then deposited upon the others, so that all increase in size."—Morgan. Hulett suggests the preparation of saturated solutions from large particles as there is less likelihood of supersaturation.

OSMOSIS.

"If a *solution* and the pure *solvent* are separated by a semipermeable membrane the solvent will flow through the membrane *into* the solution, where its *escaping tendency* is less. The only way of preventing this flow is to make the *escaping tendency* of the solvent the same on both sides of the membrane. There are two simple ways of accomplishing this, (1) to increase the pressure on the solution until the escaping tendency of the solvent in the solution is raised to equal that of the solvent in the pure state, (2) to diminish the pressure on the pure solvent until its escaping tendency is lowered to equal that of the solvent in the solution.

The osmotic pressure may, therefore, be defined in two ways, (1) as usually defined, *it is the increase in the pressure on the solution necessary to bring the latter into equilibrium with the solvent;* (2) Noyes,* however, prefers to define the osmotic pressure as *the diminution in the pressure on the solvent necessary to bring it into equilibrium with the solution.* Neither of these definitions is entirely free from objections."—Lewis, G. N.†

Experiment III.—(L. T.) Osmotic Pressure.

Note.—The instructor or assistant should assemble the apparatus (Fig. 20) in the presence of the members of the class. The use of a solu-

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* Z. physik. Chem., 35, 707 (1900).

† Osmotic Pressure of Concentrated Solutions."—Jour. Amer. Chem. Soc., 30, 668 (1908).

tion of sugar is suggested. Whether the experiment is designed to show relationships in a quantitative or qualitative manner, the effects of concentration and temperature upon the osmotic pressure should be demonstrated. These effects should be compared with corresponding effects produced on gases by similar influences. By use of the following data the possibility of applying the "gas law," PV = RT, to dilute solutions, may be shown.

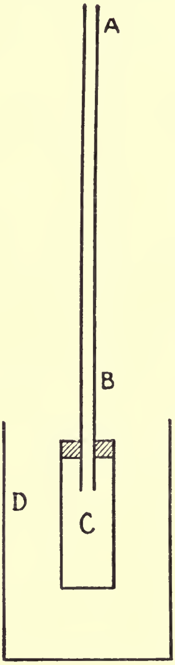

Fig. 20.

OSMOTIC PRESSURE OF CANE SUGAR.

("Osmotic Investigations"—Pfeffer,—Ames Sci. Mem's.)

Effect of Concentration.		*Effect of Temperature.*	
		(1% sol. of cane sugar.)	
Concentration in per cent. by weight.	Pressure in mm. of Hg.	Temperature.	Pressure.
1 per cent.	535 mm.	14.2° C.	510 mm.
2 per cent.	1016 mm.	32.0° C.	544 mm.
2.74 per cent.	1518 mm.		
4 per cent.	2052 mm.	6.8° C.	505 mm.
6 per cent.	3075 mm.	13.7° C.	525 mm.
1 per cent.	535 mm.	22.0° C.	548 mm.

It will be seen that Pfeffer found the osmotic pressure of a 1 per cent. sugar solution at 6.8° C. to be equal to 50.5 cm. of mercury or 50.5 x 13.59 grm. per sq. cm. A 1 per cent. sugar solution contains approximately 1 grm. of sugar per 100 cm.^{3} of solution. As the molecular weight of sugar ($C_{12}H_{22}O_{11}$) is 342, then a gram-molecular weight is contained in 34,200 cm.^{3} of the solution. This volume represents then the molar volume at 6.8° C. or 279.8° C. on absolute scale (T).

$$PV = RT,$$

$$\text{or,} \quad \frac{PV}{T} = R = 84800 \text{ gr. cms.}$$

$$\text{Substituting, } \frac{50.5 \times 13.59 \times 34200}{279.8} = 83{,}900 \text{ (approx.).}$$

OSMOTIC PRESSURE AND MOLECULAR WEIGHTS.

(Sugar Solutions at about 20° C.)
(Morse and Frazer.)

Weight normal Moles in 1000 grm. H_2O. (W)	Volume normal Moles per Liter.	Pressures at Same Temperature. Gaseous.	Osmotic (P).	$M = \frac{W(22.4 + 0.0824t)}{P}$
0.05	0.04948	1.21	1.26	327.5
0.10	0.09794	2.40	2.44	336.9
0.20	0.19192	4.82	4.78	345.2
0.25	0.23748	6.06	6.05	342.9
0.30	0.28213	7.22	7.23	342.0
0.40	0.36886	9.68	9.66	343.1
0.50	0.45228	12.07	12.09	341.7
0.60	0.53252	14.58	14.38	347.1
0.70	0.60981	17.16	17.03	344.8
0.80	0.68428	19.17	19.38	338.5
0.89101	0.75000	21.48	21.21	346.5
0.90	0.75610	21.73	21.81	340.0
1.00	0.82534	24.27	24.49	339.2
			Mean,	341.2

Van't Hoff summed up these results in the form of a law which bears his name:—"*The osmotic pressure of a substance in solution is the same pressure which that substance would exert were it in gaseous form at the same temperature and occupying the same volume.*"

In a paper which appeared in the Amer. Chem. Jour., in July, 1905, Morse and Frazer show as the result of a series of accurate experiments, that Van't Hoff's law holds for solutions of sugar if the words, "volume of the pure solvent," are substituted for the word "volume," which refers to the total volume of the solution. They say: "When we dissolved a gram-molecular weight of cane sugar (342.22 grm.) in 1000 grams of water, i.e., in that mass of *solvent* which has the unit volume, 1 liter, at the temperature of maximum density, we found its osmotic pressure, at about 20°, in quite close accord with the pressure which a gram-molecular weight of hydrogen would exert, at the same temperature, if its volume were reduced to 1 liter, i.e., to that volume which the unit mass of solvent has at the temperature of greatest density." Or in other words, a substance in solution "exerts an osmotic pressure throughout the larger volume of the solution equal to that which as a gas it would exert if confined to the smaller volume of the pure solvent."

"It should be borne in mind," says Walker, "that the osmotic pressure in a solution may be regarded as always present, whether a semipermeable membrane renders it visible or not. The osmotic pressure in the ordinary reagent bottles of the laboratory is of the dimensions of 50 atmospheres. This pressure is, of course, not borne by the walls of the bottle nor is it apparent at the free surface of the liquid. Where the liquid comes in contact with the enclosing vessel there we find a liquid surface, and a consideration of the magnitude of the forces at work in the phenomena of surface tension leads us to believe that the pressure at right angles to the free surface of a liquid, and directed towards the interior of the liquid, is measurable in hundreds and even thousands of atmospheres. Osmotic pressures, then, large as they are in ordinary solutions, are small compared to the surface pressures in liquids, and their existence is consequently not evident at the free surface of liquids. It is only when these surface pressures are got rid of that we can measure osmotic pressures directly. The liquid solvent can easily penetrate the semipermeable membrane, so at the semipermeable membrane there is no surface pressure of the ordinary type. This continuity of the liquid through the semipermeable partition gives us, therefore, the opportunity of determining differences of internal pressure in the solution and the solvent. Various hypotheses have been put forward to explain the nature of osmotic pressure, but none of them can be accounted satisfactory."

Experiment IV.—Effect of Temperature on Solubility of Solids.

(*a*) Temperature increases solubility. Add sodium chloride to a test tube half filled with water; shake and continue to add salt until no more will dissolve. The solution is said to be *saturated* at the temperature of the solution. Heat the test tube and contents; add salt until solution is saturated at the higher temperature; set tube aside to cool if there is no undissolved salt in it, otherwise, filter and observe filtrate on cooling. Is the supernatant liquid saturated at the prevailing temperature? Decant a portion of the clear liquid into another test tube; cool the contents to a lower temperature by immersing tube in a mixture of ice and water, or allow cold tap water to drip upon tube. Is more salt deposited? Is it in equilibrium with the salt in solution?

Can the equilibrium be destroyed temporarily by adding water? Try. Explain. Boil solution in test tube until salt is deposited. Explain.

(*b*) Temperature diminishes solubility. Prepare a concentrated solution of calcium citrate at the temperature of the laboratory; heat, but do not boil, as it is desired to avoid the vaporization of any appreciable amount of water. Results? Explain .

(*c*) Repeat (*b*) using calcium hydroxide.

Experiment V.—Supersaturated Solutions.

Fill a test tube of medium size nearly full of crystallized sodium sulphate; add 4 or 5 cm.^{3} of water and heat gently until solution has a temperature of about 30° C.; shake; add salt until a saturated solution is procured; pour solution into a clean, dry test tube or small flask; cover the vessel; allow it to cool, then introduce a small crystal of sodium sulphate. If solution has been prepared properly the excess of salt will crystallize out of the solution. Is the supersaturated solution a case of stable or unstable equilibrium when in contact with the solid solute?

Experiment VI.—Thermal Phenomena Accompanying the Dissolving of a Solute in a Pure Solvent.

Measure 10 cm.^{3} of water into each of five test tubes; take the temperature of the water in each tube; to the water in one of the tubes add slowly 5 grm. (see sp. gr., do not weigh) of concentrated H_2SO_4, stirring carefully with the thermometer as acid is added. When the contents of tube are homogeneous, i.e., one phase, record the reading of the thermometer; remove thermometer and clean it.

Repeat above using separately, 5 grm. of solid ammonium chloride (NH_4Cl), dehydrated $CuSO_4$, $Na_2SO_4.10\ H_2O$, Na_2SO_4. Tabulate data. Conclusions?

Experiment VII.—Relative Solubility of Solids. Effect of Temperature.

(*a*) Place 1 grm. of CuO in a test tube; add 6 cm.^{3} of water. Does it dissolve? Heat the mixture to boiling. Effect?

(*b*) To 5 grm. of NaCl add 6 cm.^{3} of water. Does the salt dissolve? Heat mixture to boiling in an endeavor to dissolve all of the salt. Are you successful? Pour the hot saturated solution upon a *dry* filter; collect the filtrate in a test tube and cool. Results? Explain.

(*c*) Pulverize about 15 grm. of $K_2Cr_2O_7$; to 5 grm. in a test tube add 6 cm.^{3} of water. Will all of the solid dissolve in the solvent? Heat mixture to boiling. Has all of the solid dissolved? Cool the solution. Observe the effect of lowering the temperature.

Note.—The pulverized $K_2Cr_2O_7$ will be needed in Exp. VIII.

Experiment. VIII.—(Quant.) Prepare a saturated solution of $K_2Cr_2O_7$; to 8 grm. of the powdered substance in a flask or beaker, add 50 cm.^{3} of distilled water; assist the process of dissolving by frequently shaking it. If the directions have been adhered to the solution will probably be saturated at the end of 10 min. Take the temperature of the solution. Into a weighed evaporating dish, weigh accurately 20–30 grm. of the solution; evaporate to dryness; cool; weigh. Repeat heating and weighing. Calculate the weight of dichromate in 1 liter of the solution (saturated) at the observed temperature. How many gram-molecules (moles) of potassium dichromate in a liter of the saturated solution?

Terminology of Solutions.—When a substance dissolves in a liquid there is for each temperature and pressure a definite *solubility*, i.e., a definite relation between the solute and the solvent. If the solution contains less of the solute than corresponds to the latter's solubility in the solvent, it is *unsaturated;* if the amount in solution is in excess of the amount required to saturate it, the solution is said to be *supersaturated.* The test of the degree of saturation of a solution is made by placing a portion of the solid solute in contact with it; if the solution is unsaturated, a portion of the solute will dissolve; if supersaturated, a portion of the solute will separate from the solution, and continue to be deposited until the solution is saturated and a condition of stable equilibrium is established.

Although the above nomenclature is convenient it does not convey the definite information which is so much desired by the chemist. Because of this, the *concentrations* of solutions are frequently expressed in terms of physical or chemical units.

The *concentration* of any substance is the total amount of that substance in solution in a unit volume.

The *solubility* of a substance is expressed in terms of the number of *grams* or *gram-molecules* which can be dissolved in a unit volume at a given temperature and pressure.

A solution is referred to as being *standard* when its concentration is known. Of more frequent use, however, are the terms, *normal solutions* and *molar solutions.*

A *normal solution* is a standard solution which contains in one liter the hydrogen equivalent of the active reagent, expressed in grams. Thus a normal solution of HCl contains 36.45 grams of hydrogen chloride; normal H_2SO_4, $\frac{\text{Mol. Wt.}}{2}$ grams; normal KOH, $\frac{\text{Mol. Wt.}}{1}$ grams; normal iodine, 126.97 grams in a liter. If a liter contains $\frac{1}{10}$ of an equivalent weight it is designated tenth or deci-normal (.1N); if $\frac{1}{100}$ of an equivalent, hundredth or centi-normal (.01N).

A *molar solution* is a standard solution which contains one *mole* or one *gram-molecular* weight of the solute in one liter of solution. Thus a *molar* solution of HCl contains 36.45 grm. of hydrogen chloride; molar H_2SO_4, 98.07 grm.; molar NaOH, 40.05 grm. of sodium hydroxide.

Influence of Temperature On Solubility of Solids.—It is a general rule, if the temperature changes, the solubility changes. The solubility of the majority of solid substances increases with increase of temperature; however, there are cases in which the solubility is decreased by rise of temperature. The increase in the solubility of potassium chloride is approximately proportional to the increase of temperature. The solubility of calcium citrate is greater at 10° C. than it is at higher temperatures, say 70° C.; the same is true of calcium hydroxide. It is quite probable that in the majority of cases there is a fall of temperature due to the mere act of solution, but the heat of the chemical combination which undoubtedly follows the process of dissolving in many instances, is frequently so much in excess, that heat alone is the observed result of solution. For example, when sulphuric acid is dissolved in water, it combines with the water to form hydrates of sulphuric acid and a large quantity of heat is developed; the same conduct is displayed by dehydrated salts, like Na_2CO_3 and Na_2SO_4. The question, is there a relation between the influence of temperature upon solubility, and some other property of substances, may be answered by an application of that principle which is the basis of explanation of all influences affecting equilibrium; the principle referred to is the one enunciated in the form of La Chatelier's Theorem. If a substance dissolves with an absorption of heat, its solubility will increase with rise of temperature; if, on the other hand, heat is developed on solution, solubility will decrease with rise of temperature. When substances dissolve without thermal alterations, solubility is practically independent of temperature. The solubility of sodium chloride is affected but little by temperature alterations. A simple test of the influence of temperature upon the solubility of a given substance in a particular solvent may be made by preparing a saturated solution at a given temperature, then observe if increase in temperature causes deposition of the solid; if solute is not deposited, add a small crystal of it to the solution; in case of supersaturation the solid will deposit from the solution, and if the solution is now unsaturated, as the result of the rise in temperature, the crystal will dissolve.

TABLE OF SOLUBILITY OF SOLIDS.

(Grams dissolved by 100 cm.³ of water.)

	At 0° C.		10° C.		100° C.		(Parts dissolved by 100 parts of 80% alcohol at 15°.)
Sodium Chloride........	35.6	grm.	35.63	grm.	39.9	grm.	1.22
Sodium Nitrate..........	72.9	"	87.5	"	180.0	"	2.8
Sodium Sulphate (hydrated)............	5.02	"	55.0 (32.38° C.)	"	42.4 (anhydrous)	"	1.3 (sp. gr. .94)
Potassium Chloride.....	30.0	"	34.7	"	56.6	"	0.45 (70%)
Potassium Nitrate......	13.3	"	29.0 (18° C.)	"	247.0	"	0.4
Potassium Sulphate.....	8.46	"	10.9	"	26.2	"	0.21 (40%)
Potassium Dichromate ..	4.9	"	13.1	"	102.0	"	——
Ammonium Chloride....	28.4	"	37.28	"	72.80	"	12.0 (abs. 8°)
Copper Sulphate	18.2	"	42.31	"	203.22	"	——
Calcium Hydroxide.....	0.174	"	0.13	"	0.08	"	——
Calcium Sulphate.......	0.205	"	0.208	"	.218	"	——
Calcium Chloride.......	49.59	"	74.00	"	149.98	"	60.00 (abs. 80°)

Heat of Solution.—We have observed that the process of solution is usually accompanied by thermal phenomena, i.e., heat is absorbed or evolved. This is called the *heat of solution.* It is obvious that for different amounts of water, this will vary; in order to establish uniformity, the heat of solution is now usually understood to be the amount of heat liberated or absorbed by the solution of 1 gram-molecule of the substance under consideration, in such a large quantity of water (solvent) that the further addition of water will not yield an additional heat effect. The addition of the first quantity of water to the solute produces a relatively larger thermal change than the succeeding additions of equal amounts of the solvent, therefore the use of an unlimited volume of the solvent as suggested above.

Ostwald defines the "heat of solution" as "*the heat which is taken up or given out when a further quantity of salt is dissolved in a solution saturated at a definite temperature.*" "This quantity of heat," he says, "must not be confused with that which accompanies the solution of a salt in the *pure* solvent, and which is usually what is measured. In the case of difficulty soluble substances, it is true, the two are not greatly different; but where the substances are soluble in large amounts, they can have not only a different value but even a different sign." Richards, T. W., defines the "heat of solution," of a substance, as that which is developed or absorbed when the final quantity (1 mole) of salt which finishes the saturation of an unlimited quantity of water, is added. An erroneous application of this principle has led to many apparent and perplexing contradictions.

The following tables give the heat of solution of a number of substances in a large quantity of water at 18°–20° C. This is designated by the addition of the abbreviation Aq (aqua) to the formula or symbol of the substance:

HEAT OF SOLUTION OF SOLIDS.

(From Hortsmann, Theoret. Chem., p. 502.)

$NaOH$, Aq = +9780 cal.
$NaCl$, Aq = —1180 cal.
Na_2CO_3, Aq = +5640
$Na_2CO_3.10\ H_2O$, Aq = —16160
Na_2SO_4, Aq = +460
$Na_2SO_4.10\ H_2O$, Aq = —18760
$NaC_2H_3O_2$, Aq = +4200
$Na\ Br$, Aq = —190
$Na\ Br.2H_2O$, Aq = —4710
$C_{12}H_{22}O_{11}$, Aq = —800

KOH, Aq = +12500 cal.
$KOH.2H_2O$, Aq = —30 cal.
KCl, Aq = —4440
K_2SO_4, Aq = —6380
NH_4Cl, Aq = —3880
$LiCl$, Aq = +8440
$CaCl_2$, Aq = +3258
$AgCl$, Aq = —15800
$Ag\ Br$, Aq = —20200
$Ag\ I$, Aq = —26600.

HEAT OF SOLUTION OF LIQUIDS.

H_2SO_4, Aq = +17800 cal.
$C_2H_4O_2$, Aq = +420 cal.
$(C_2H_5)_2O$, Aq = +5940 cal.

CH_3OH, Aq = +2000 cal.
C_2H_5OH, Aq = +2540 cal.
C_3H_7OH, Aq = +3050 cal.

HEAT OF SOLUTION OF GASES.

H_2F_2, Aq = +11800 cal.*
HCl, Aq = +17310 cal.
HBr, Aq = +19940 cal.
H I, Aq = +19210 cal.
Cl_2, Aq = +4870 cal.
CO_2, Aq = +5880 cal.
NH_3, Aq = +8430 cal.

All gases which have been examined, and all liquids, as a rule, dissolve with evolution of heat, but solid substances show no such uniformity of conduct. Some of them, solids, dissolve with an absorption of heat while others behave in a contrary manner. Nernst suggests that the explanation of this is simple. Assume that a given substance in the gaseous condition always dissolves with an evolution of heat, then if it is reduced to the liquid state before it is placed in solution, it will dissolve with an evolution or absorption of heat according as its heat of vaporization is less or greater than its heat of solution. The sign of the heat of solution of the substance in the solid phase will depend upon the relative magnitude of its heat of sublimation and its heat of solution when in the gaseous phase. Interpreting the data presented by the above tables in the light of the above suggested explanation, we conclude that the "heat of solution in the gaseous state is always greater than the heat of vaporization, but it is usually smaller than the heat of vaporization plus the heat of fusion, i.e., it is smaller than the heat of sublimation."

Effect of Pressure on Solubility of Solids.—A solution usually occupies less space than the sum of its components; it never occupies more than the sum. In some cases, for example, solutions of Li(OH), $Ba(OH)_2$, $NiSO_4$, $CaSO_4$, the volume of the solution is less than the original volume of the solvent. Inasmuch as the process of solution is frequently accompanied by small changes in volume, it is evident that if a solution is in equilibrium with the solid substance, pressure will alter the solubility in a manner which may be anticipated by the application of the principle enunciated in Le Chatelier's Theorem. The effect of pressure is so small that pressures equivalent to hundreds of atmospheres are required to effect a change in solubility so small that it can scarcely be measured.

The question may arise, what is the explanation of these volume-changes observed while preparing solutions; why does alcohol (ethyl) and water when mixed in equal proportions by volume, contract about 3 per cent. of the total volume? Why do 10,000 $cm.^3$ of water and 27.5 $cm.^3$ (58.5 grm.) of sodium chloride yield a solution whose volume is about 10016.5 $cm.^3$? The question can not as yet be answered definitely. It has been suggested that the "associated" molecules of the water are broken up during the dissolving of the solute, and as the molecules occupy less space when in a "non-associated" condition, this may account for the observed contraction. Again, it may be due to the fact that the dissolved substance undergoes hydration, i.e., *attracts* water to itself, forming a hydrate. Now the water in hydrated salts occupies less space than when not thus combined. This may partially

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* 580 cal. (ext. work) should be subtracted from above figures.

explain the conduct of the solutions referred to above as examples in which the volume of the solution was less than original volume of solvent. Just where the contraction is no one seems to know.

Solubility of Liquids.—It is frequently convenient, when speaking of the relative solubility of liquids in liquids, to refer to the solubility of "pairs of liquids." These groups of two many be divided into four orders:

SOLUBILITY OF PAIRS OF LIQUIDS.

1.—Miscible in all proportions.
2.—Partially miscible.
3.—Immiscible (mutually insoluble).
4.—Pairs which are in one order at some temperatures but in another order at other temperatures.

The first order embraces those pairs in which the solubility of the two liquids in each other is unlimited; the second order, those pairs in which the solubility of the two liquids in each other is limited; the third order, those pairs in which the two liquids are not wholly but practically insoluble in each other, as mercury and water, organic liquids and water, etc.; the fourth order, explains itself, and suggests that orders, one, two and three, will pass gradually from one to the other with sufficient change of temperature.

Experiment IX.—Relative Solubility of Liquids.

(*a*) To 5 $cm.^3$ of water in a test tube add a few drops of alcohol; shake. How many phases are present? Do alcohol and water mix? Add alcohol in small quantities until 5 $cm.^3$ of alcohol have been added? Does the mixture become homogeneous on shaking after each addition of alcohol? To which order does the above pair of liquids belong, basing your answer on observed results?

(*b*) Repeat (*a*) using 5 $cm.^3$ of ether.

(*c*) Repeat (*a*) using 2 $cm.^3$ of kerosene.

(*d*) Repeat (*a*), using 2 $cm.^3$ of benzol or toluol. Define "phase."

Experiment X.—Mutual Solubility of Liquids.

To 3 $cm.^3$ of distilled H_2O in a test tube add 3 $cm.^3$ of ether and shake vigorously. How many phases are present? Does each layer represent a solution? Set tube aside—to be used later. To 3 $cm.^3$ of ether add 3 $cm.^3$ of distilled H_2O. Proceed as above. Compare the contents of the two test tubes. Pour the contents of one tube into the other tube, thereby mixing the solutions; allow tube to stand until there are two distinct phases, i.e., two layers. Dehydrate about a grm. of pulverized $CuSO_4.10\ H_2O$, the salt should be nearly white. Now devise a method for proving that the top layer of the solution in the test tube is a solution of water in ether. Also prove that ether is present in the lower layer which is a solution of ether in water.

Hint.—When a solution of ether and water is gently heated in a test tube, the ether is rapidly expelled and can be inflamed.

The heavier liquid at the bottom of the test tube is an aqueous solution of ether containing about 10 per cent. of ether; the upper layer is an etheral solution of water containing about 3 per cent. of water. A similar phenomenon is exhibited by the use of a concentrated solution of potassium carbonate and aqueous ammonia, sp. gr. 0.88. This is probably the only known case in which aqueous solutions of inorganic substances behave in this manner.

Experiment XI.—Effect of Temperature. Critical Solution Temperature.

(*a*) Increase in temperature produces complete miscibility. To a test tube containing about 3 cm.^{3} of solid or liquid phenol* add about 10 cm.^{3} of water; cork the tube and shake vigorously; a milky appearing mixture, an *emulsion*, is the result; allow the tube to stand for some time, or better, remove the cork and heat gently—when the mixture will separate into layers—an aqueous solution of phenol above, and a solution of water in phenol below; now place the test tube in the flame and heat gradually until the line of demarcation between the two phases slowly disappears; warm a thermometer until its reading is about 80° C., then introduce it into the test tube so that its bulb will be immersed in the contents, and determine the temperature at which the mixture becomes homogeneous; cool the tube and note the reading of the thermometer when the milky appearance is observed. Take the average of the two thermometer readings. What are your conclusions as to the mutual solubility of this pair of liquids at the temperature at which the contents became homogeneous? At the temperature of the laboratory (20° C.)?

(*b*) Lowering of the temperature produces complete miscibility. Use dimethylamine and water. (Instructions.)

The lowest temperature at which pairs of liquids like phenol and water become miscible in all proportions is called the "*critical solution temperature.*"

Experiment XII.—Distribution of Solute Between Two Immiscible Solvents. Law of Distribution.

To a small flake of sublimed iodine in a test tube add 10 cm.^{3} of distilled H_2O; shake it vigorously for several minutes as the iodine is nearly insoluble and dissolves slowly; pour off the clear solution into a clean test tube. Repeat above operation using an aqueous solution of KI as the solvent. Divide each solution into two portions; to one portion of each solution add 3 cm.^{3} of ether; and to the other portion of each, add 3 cm.^{3} of carbon disulphide; shake the tubes. Results? In each case, after adding ether or carbon disulphide, how many phases were present in the respective test tubes? Drawing your conclusions from

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* Caution:—A very small quantity of phenol (carbolic acid, C_6H_6O) will attack the flesh. Handle vessel containing it with the utmost care.

observed results, arrange the solvents in the order in which the increasing solubility of iodine is shown.

Law of Distribution.—*The solute is distributed between the two solvents in such a way that the ratio of its concentration in each is a constant.* This constant is practically independent of the absolute concentration and is dependent only upon temperature and the nature of the solute and the two solvents. (It is obvious that the ratio of the concentrations is the ratio of the solubilities in the separate solvents.) Also, if two or more substances are placed in solution the coefficients of distribution are the same as if each substance were present alone. (This reminds one of the analogous conduct of gases.) In connection with the above experiment, it may be noted that in 1 $cm.^3$ of the carbon disulphide solution there will be found 600 times as much iodine as in 1 $cm.^3$ of the aqueous solution of iodine.

Experiment XIII.—Pressure of Gas Affects Solubility.

Half fill the large test tube which you used in generating oxygen, with water; cork the tube with a rubber stopper perforated with a single hole; shake the tube until the water is saturated with air; connect tube with an air pump and exhaust the air from above the solution; observe the small bubbles of gas passing out of the liquid. Explain. What would be the probable effect of increasing the pressure of the gas?

Henry's Law.—*At a constant temperature, a given quantity of the liquid solvent will dissolve weights of a gas which are proportional to the pressure of the gas.* This law holds when the gases are only moderately soluble. When a mixture of gases dissolves in a liquid, each dissolves as if it were present alone—i.e., each dissolves according to its own *partial pressure.* In other words, the gas distributes itself between the liquid and gaseous phases according to a constant (K) which is a characteristic of each gas. (Recall the Law of Distribution.)

Experiment XIV.—Effect of Solvent on Solubility.

Half fill a test tube with water; observe that it is perfectly clear; add 5 $cm.^3$ of alcohol. Explain the liberation of the small bubbles of air.

SOLUBILITY OF GASES.

(0° C. 760 mm.)

Name of gas.	1 Vol. of H_2O Dissolves,	1 Vol. of C_2H_6O Dissolves,
Hydrogen	0.02 vols.	0.07 vols.
Oxygen	0.04 vols.	0.28 vols.
Nitrogen	0.02 vols.	0.13 vols.
Carbon dioxide	1.79 vols.	4.32 vols.
Hydrogen sulphide	4.37 vols.	17.9 vols.
Ethylene	0.25 vols.	3.6 vols.
Ammonia	1148.80 vols.	——
Hydrochloric acid	505.00 vols.	——

Experiment XV.—Effect of Temperature on Solubility.

Half fill a 1000 cm.^{3} flask with water; cork it and shake it until water is saturated with air; determine its temperature. Calibrate a 300 cm.^{3} flask; provide it with a rubber cork through which passes a delivery tube which will dip beneath the surface of the water in the pneumatic trough; fill the 300 cm.^{3} flask and delivery tube with the water saturated with air; heat the flask to boiling; collect the air which is liberated in an inverted eudiometer by water-displacement; read the barometer, determine the temperature of the water in the trough, equalize the water levels and take the reading of the eudiometer. Calculate the volume of gas dissolved by a cm.^{3} of water under the conditions which prevailed while preparing the aqueous solution of air.

Note.—A test tube may be used in place of the eudiometer by marking the volume of gas with gummed paper, and then calibrating the tube.

SOLUBILITY OF GASES.

(Vols. of gas which 1 vol. of H_2O will dissolve.)

Temperature.	Hydrogen.	Oxygen.	Nitrogen.	Carbon dioxide.
0°	.0215 vol.	.0411 vol.	.0203 vol.	.0179 vol.
5°	.0206 vol.	.0362 vol.	.0179 vol.	.0144 vol.
10°	.0198 vol.	.0325 vol.	.0160 vol.	.0118 vol.
20°	.0185 vol.	.0283 vol.	.0140 vol.	.0090 vol.

The quantity of gas which a liquid is capable of dissolving depends upon, (1) nature of solvent; (2) nature of gas; (3) the temperature of the solvent; (4) the partial pressure of the gas.

Gases with reference to each other, are regarded as being miscible in all proportions. Inasmuch as solids and liquids directly vaporize into gases, the latter are considered as solvents of the former.

Experiment XVI.—Lowering the Vapor Tension or Elevation of the Boiling Point.

Determine the boiling point of distilled water—proceed as in a former experiment. In this case determine the temperature of the liquid as well as that of the vapor. Record your data. Add a sufficient quantity of $CaCl_2$ to nearly saturate 20–25 cm.^{3} of the distilled water; heat the solution to boiling. Observe, (*a*) the temperature of the solution; (*b*) the temperature of the vapor. Record data. Explain. Will vegetables cook more rapidly in a boiling salt solution than in boiling distilled water? Why?

Caution.—Suspend the thermometer when taking temperatures; do not allow it to touch the flask.

Experiment XVII.—Depression of the Freezing Point.

Half fill a test tube with distilled water; determine its freezing point; add NaCl until the water is nearly saturated; determine the freezing point of the solution. Has the freezing point of the water been depressed? How much (express in degrees° C.)? (See Fig. 21, Beckmann apparatus.)

Elevation of the Boiling Point.—It has been known for many years that the normal boiling or freezing point of a liquid may be altered by dissolving a quantity of a solid substance in it. We have observed that pure water freezes at 0° C. and boils at 100° C. (760 mm.), whereas the freezing point of *solutions* of solids is below, and the boiling point above, normal. If the boiling point of a solvent is elevated, it is obvious that its vapor tension is lowered by the presence of the solute.

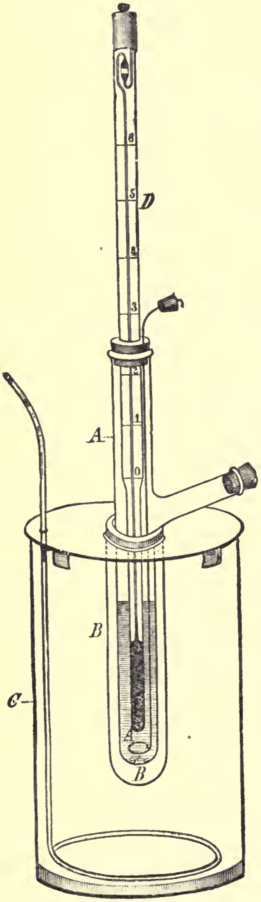

FIG. 21.

It has been shown experimentally that a definite relation holds between the freezing and boiling points of a liquid and the quantity and nature of the dissolved substance. Further, the *degree* of the depression of the freezing point or the elevation of the boiling point depends upon four factors: (1) the nature of the solute; (2) the quantity of the solute; (3) the nature of the solvent; (4) the quantity of the solvent. To make an application—1 gram of salt dissolved in 100 grams of acetic acid produces a depression of the freezing point which is different from that produced by dissolving the same quantity of salt in 100 grams of water.

One mole of any substance dissolved in 100 grams of solvent must always produce a certain definite increase in the boiling point of that solvent, because it produces a definite depression of the vapor tension. (Recall relation of osmotic pressure to vapor pressure.)

The elevation produced by 1 gram of substance in 100 grams of solvent is spoken of as the *specific elevation* (d). It has been found that the specific elevation (d) produced by *any* substance in any *given solvent* when multiplied by the molecular weight (M) of the solute, gives a product which is practically a constant (K) for that particular solvent. K represents the *molecular-increase* of the boiling point, i.e., "that due to the solution of 1 mole of substance in 100 grams of solvent, which must be constant for all substances in the *same solvent*."

$$K = dM, \qquad M = \frac{K.}{d}$$

One mole of any substance dissolved in 100 grams of ether increases the boiling point of the latter 21.10° C.

Ostwald (Physico-Chemical Measurements) gives the following values for the constant K which is equal to 100 K.:—

Ethyl ether	2110	Ethyl acetate	2610
Benzene	2670	Acetone	1670
Chloroform	3660	Water	520
Carbon disulphide	2370	Ethylene dibromide	6320
Acetic acid	2530	Aniline	3220
Ethyl alcohol	1150	Phenol	3040

The following expression has been developed for the purpose of ascertaining molecular weights:

$$d = \frac{\triangle G}{100g},$$

$$M = 100\ K \frac{g}{\triangle G},$$

where G represents the number of grams of solvent; g, the grams of solute; △ the elevation of the boiling point in degrees, and M, the molecular weight of the solute. The value of K may also be found by a process of reasoning based upon thermo-dynamical principles.

Beckman while determining the molecular weight of iodine in ether recorded the following data:

$$K = 21.10, \quad g = 2.0579, \quad G = 30.14, \quad \triangle = 0.566;$$

$$M = 100\ K \frac{g}{\triangle G}.$$

substituting in above equations,—

$$M = 100 \times 21.10 \frac{2.0579}{0.566 \times 30.14}$$

$$M = 254,$$
$$I_2 = 254.$$

Morgan suggests the use of the following simple proportion in calculating the molecular weight:

$$21.1 : 0.566 :: M \text{ grm. per } 100 \text{ grm.} : \frac{2.0579}{30.14} \times 100.$$

$$M = 254.$$

Depression of the Freezing Point.—Using a similar method of calculating experimental data, we are able to ascertain the molecular weight of the solute by observing the depression of the freezing point of the solvent. In 1887 Raoult found that "1 *mole of any substance dissolved in* 100 *grams of any one solvent causes a constant depression of the freezing point.*" It will be observed that the relation of the solute to the freezing point is very similar to its relation to the boiling point. The mathematical form of the expression used to calculate the molecular weight is identical with the above. If d equals the *specific depression* and K the *molecular depression*, then,—

$$K = dM, \qquad M = \frac{K}{d}.$$

$$d = \frac{\triangle G}{100g},$$

$$M = 100\ K \frac{g}{\triangle G},$$

where G represents the number of grams of solvent; g, the grams of solute; $\triangle$ the depression of the freezing point in degrees, and M the molecular weight of the solids.

SOLVENTS.

Acetic Acid.				Water.			
Solute.	d.	M.	K.	Solute.	d.	M.	K.
SO_2	0.6015	64	38.5	NH_3	1.1705	17.	18.80
CS_2	0.5050	76	38.4	$CuSo_4$	0.1153	159.7	18.41
$CH\ Cl_3$	0.3247	119.3	38.8	$C_2H_4O_2$	0.3162	60.	18.97
		Aver.	38.6			Aver.	18.72
		(Ostwald),	38.8			(Ostwald),	18.90
						(Jones),	18.50

SOLUTIONS IN WATER.

(Jones, Phys. Chem.)

Solute. (Organic.)	Molecular. Lowering (K).	Solute. (Inorganic.)	Molecular. Lowering (K).
Methy alcohol	17.3	Hydrochloric acid	39.1
Malic acid	18.7	Sodium oxalate	13.2
Acetone	17.1	Sodium hydroxide	36.2
Acetic acid	19.0	Sulphuric acid	38.2

RAOULT'S LAW FOR SOLVENTS.

(Raoult's Tables).

Solvents.	M Mol. Weight.	K Mol. Lowering.	K/M Lowering produced by 1 molecule in 100 molecules.
Formic acid	46	29	0°.63
Acetic acid	60	39	0°.65
Benzene	78	50	0°.64
Ethylene bromide	123	73	0°.59
Water	18	47	2°.61

Raoult's Law.—"*If one molecule of any substance is dissolved in one hundred molecules of any liquid of a different nature, the lowering of the freezing point of this liquid is always nearly the same, and approximately* 0°.63—" Sci. Memoirs. The above table makes apparent the real meaning of Raoult's Law. It also suggests, that inasmuch as the molecular-lowering of water, which in a number of cases is as great as 47 and is an exception to the law, that its molecular weight is probably greater than 18. Ramsay and Shields, from a study of the surface-tension of water, reached the conclusion that the molecular formula for water in the liquid state should be $(H_2O)_4$ or H_8O_4. This conclusion is confirmed by the freezing point lowerings of water produced by dissolved substances.

The value 2° .61, $\left(\frac{K}{M}\right)$,

indicates that the weight of solvent used, contained only one-fourth of the number of molecules required, or in other words, each molecule weighed four times as much as calculated. Assuming that the weight of the molecule should be 18 x 4 = 72, and inserting this value in the equation,

$$\frac{K}{M} = (0°.63, \text{Aver.}), \text{ we have } \frac{47}{18 \times 4} = 0°.65.$$

This value is very close to the other values of the table.

It should be remembered that Raoult's Law is only an approximation, but one of much value in correlating many facts.

Experiment XVIII.—Lowering of the Solution Tension.

Half fill a 250 cm.³ or 500 cm.³ flask with distilled H_2O; (The flask should have a long narrow neck) saturate the water with ether; add H_2O and ether repeatedly until flask contains a saturated aqueous solution of ether which rises into the neck of the flask for a distance of about 2 cm.³; there should be a layer of ether about 1 cm. in thickness above the aqueous solution. The height of each should be marked with pieces of gummed labels. Now add 3 or 4 cm.^{3} of benzol, or toluol, either of which is quite soluble in ether; mark its height on neck of flask; shake vigorously for a minute (avoid spilling the contents of the flask); allow flask to stand undisturbed for a few minutes. Observe the height of the aqueous solution. Note the thickness of the layer of ether. Is there more or less ether in solution in the water than there was before adding the benzol to the ether? Why did the layer of ether increase in thickness by the process?

The answer to the question as to whether the process of solution is to be regarded as purely chemical or physical must be delayed until such time as the evidence shall preponderate for one or the other of the two views, which is certainly not the case with our present information. The question has been much discussed, and because of the alteration in value of well defined properties of a substance when it is dissolved in a liquid, there are many chemists who regard solution as a chemical process. As a rule, the sum of the values of a property common to solute and solvent is not the value of this property for the solution. Thermal and volume relations, solutions of constant boiling point, hydration and other phenomena which appear during the dissolving, point to the existence of a certain affinity between solute and solvent. There is little doubt but that the two react and influence each other's properties, but as to the origin and nature of this influence chemists are unable to offer a probable explanation.

Those chemists who maintain that solution should not be regarded as a chemical process point to the conduct of the solute in dilute solutions, with respect to its volume, temperature and pressure relations, i.e., the applicability of the gas law. In such cases the influence of the solvent may be neglected altogether. Again, we find that the quantity of a solid which a liquid will dissolve varies with temperature; such variation in the composition of chemical compounds is unknown. The impossibility of expressing the concentration of saturated solutions in terms of integral multiples of the chemical combining weights, and the easy recovery of the solid solute by evaporation, together with the above mentioned phenomena tend to suggest that the process of dissolving is physical.

The subject of solutions will be discussed in a future chapter.

PROBLEMS.

1.—How many grm. of KOH will be required to prepare 500 cm.^{3} of a 1 N solution? An .01 N solution? A 5 N solution?

2.—Calculate the relative number of grm. of each solute in normal solutions of H_2SO_4, HCl, H_3PO_4. In 3 N solutions. In 2 N solutions.

3.—How many grm. of HNO_3 in 1000 cm. of a 5 per cent. solution (aqueous)? If 10 grm. of NaOH are dissolved in sufficient H_2O to give a 5 per cent. solution of the solute, what was the total volume of the solution?

4.—How many cm.^{3} of water will have to be added to 10 grm. of H_2SO_4 (sp. gr. 1.84) to yield a 10 per cent. solution of acid?

5.—If 1 l. of H_2O absorbs 1 l. of CO_2 at 0°, 760 mm. how many grams of CO_2 gas are contained in a bottle of carbonic water holding 200 cm.^{3} of solution, the pressure being 5 atmospheres?

6.—The approximate composition of air is 30.9 per cent. of O, and 79.1 of N, by volume. At 15° water absorbs 0.0299 volumes of O and 0.0148 of N, the pressure of each being that of the atmosphere. What is the composition of air absorbed in H_2O?

Ans. By volume, 34.8 per cent. of O and 65.2 per cent. of N.

7.—The increase in the boiling-point of 54.65 grm. of CS_2 caused by the addition of 1.4475 grm. of P is 0°.486. What is the molecular weight of P in CS_2? What is the molecular formula if the atomic weight is 31?

8.—The molecular weight of a substance is 60. If 10 grm. of this substance is dissolved in 100 grm. of a solvent, the increase in the boiling point is 0°.87. Calculate the molecular increase in the boiling point.

9.—Find the molecular weight of oxime, $(CH_3)_2$ CNOH, if 0.284 grm. of it causes a decrease of 0°.155 in the freezing point of 100 grams of glacial acetic acid.

10.—A student working in this laboratory tabulated the following data while determining the molecular weight of turpentine by the "boiling point method." Boiling point of pure solvent (ether) as indicated by a Beckmann thermometer, 3°.25; weight of solvent 18.45 grm.; weight of turpentine, 0.865 grm.; boiling point of solution, 3°.96. Calculate the molecular weight of ether.

11.—The following data was recorded while determining the molecular weight of sugar by "freezing point method."

Freezing point of pure H_2O, (Beckmann) 5°.475,

Freezing point of solution after adding 1 gram of sugar to 20.09 grams of H_2O, 5°.198. Calculate the molecular weight of sugar.

CHAPTER XII.

ACIDS, BASES AND SALTS.

NOMENCLATURE.

CHLORINE.

Symbol, Cl. At. Wt. 35.45.

Chlorine is an elementary substance belonging to the class of "non-metals." Under ordinary laboratory conditions it is a heavy, greenish-yellow gas which possesses an irritating odor and poisonous properties. It was discovered by Scheele in 1774, who prepared it by heating hydrochloric acid with the oxide of manganese. Davy, however, proved its elementary nature and gave it its name in 1810. It possesses a great deal of chemical energy, i.e., shows great tendency to react chemically with other substances, therefore, it is not found in nature as *free* chlorine. Observe during the performance of the following experiment whether chlorine possesses the physical properties characteristic of metals.

Experiment I.—Preparation of Chlorine.

Arrange a 300 cm.^{3} flask (Fig. 22) provided with funnel tube and a delivery tube, so that it connects with washing bottle which should be about one-fourth full of concentrated sulphuric acid. The flask should be placed on a piece of iron gauze resting on a ring clamp or tripod so that flask may be heated. Introduce into flask 20 grams of manganese dioxide (MnO_2), preferably in the powdered condition. Place six clean dry bottles of about 150 cm.^{3} capacity on your desk and cover each with a glass plate or a sheet of heavy damp paper; procure from the assistant a little powdered antimony on a watch glass, a strip of bright colored calico, some litmus paper; write your name with ink upon a piece of paper, 4 or 5 cm.^{3} of turpentine in a test tube and a test tube half filled with distilled water; then arrange your hydrogen generator so that you can provide a hydrogen flame on short notice. Now add by means of funnel tube, sufficient concentrated hydrochloric acid to cover the MnO_2 in flask; be sure that lower end of funnel tube is dipping into acid; heat flask very gently; by means of a delivery tube bent at right angles and attached to the wash bottle so that it can be inserted into the mouth of a bottle, collect gas by vertical displacement of air. When bottle presents a greenish-yellow appearance remove it and cover its mouth with glass plate or damp paper. Repeat operation until six bottles have been filled with the gas and water in test tube has been saturated with chlorine. Then proceed with the following experiments. The equation for the above reaction may be written as follows:

$$MnO_2 + 4\,HCl \rightarrow MnCl_4 + \overline{Cl_2} + 2H_2O.$$
$$MnCl_4 \rightarrow MnCl_2 + \overline{Cl_2}.$$

Is chlorine lighter or heavier than air? If a liter of hydrogen weighs .0899 grams under standard conditions what will the same volume of chlorine gas weigh under identical conditions?

Experiment II.—Properties of Chlorine.

(*a*) Bleaching properties. Into a bottle of gas insert pieces of dry calico, litmus paper and paper with carmine ink upon it; set it aside for fifteen or twenty minutes. Repeat above operation with another bottle of chlorine, but moisten the articles before inserting them. Examine before leaving laboratory. Results? Compare with result when articles were perfectly dry. What conclusion would you draw? It should be observed that organic material is the basis of the coloring matter present in above specimens.

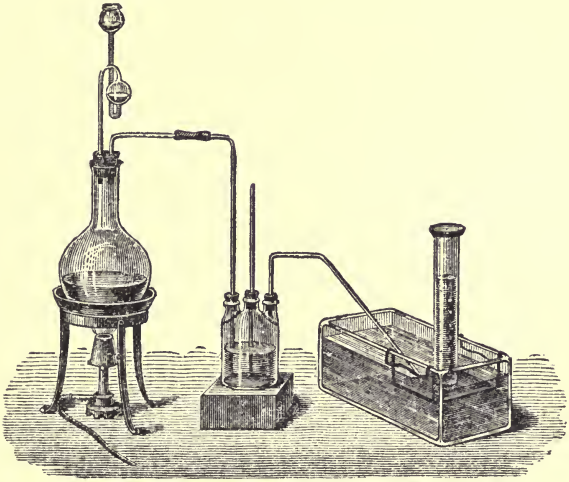

FIG. 22.

(*b*) Combination of antimony and chlorine. Into a bottle of the gas, drop a pinch of powdered antimony. Result? Place another portion of the powder in a test tube and heat it until quite warm, then quickly introduce it into the same bottle of gas. Result? What factor induced the reaction? The valency of antimony is three, that of chlorine is one. Write the equation for reaction.

(*c*) Affinity of chlorine and hydrogen.

Insert "hydrogen flame" into a bottle of chlorine (Fig. 23). Result?

Hold a piece of moist blue litmus paper just outside of mouth of bottle while "flame" is present on inside. Result? Hold another piece of blue litmus paper near the mouth of the reagent bottle labeled "hydrochloric acid." Results? What are your conclusions as to the gas formed by the burning of chlorine in hydrogen? Write equation for reaction.

Was light and heat evolved as the result of the reaction? What was probably the main source of this energy? Was it an endo- or exothermic reaction? Interpret following equation:

H, (1 gram) + Cl, (35.45 grams) $\rightarrow$ HCl, (36.45 grams) + 22,000 cals.

(*d*) Chemical action on turpentine ($C_{10}H_{16}$).

Place a strip of filter paper in the test tube containing the $C_{10}H_{16}$ and heat tube gently until it is warm. Turpentine is very inflammable. Introduce paper saturated with warm turpentine into a bottle of chlorine gas. Result?

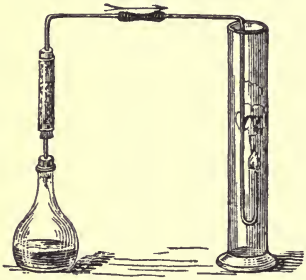

FIG. 23.

If you were told that the black appearance of paper was due to free carbon (soot) what would be your conclusion? Equation?

(*e*) Substituting power of chlorine.

1. Make a few strips of "test paper" by dipping pieces of filter paper in a solution of potassium iodide (KI) with which a clear solution of starch has been mixed. *Free* iodine will impart a blue or bluish-black color to starch. Upon a strip of test paper pour a few drops of the water saturated with chlorine. Results? Conclusions? Equation?

2. Pass hydrogen sulphide (H_2S) through a water solution of chlorine and observe effect. Before passing the H_2S into the solution notice the action of the latter upon litmus paper, both red and blue. Compare the result with a similar test made after the H_2S has been passed into it. In view of observed data, how would you explain results? Equation?

3. Optional. (L. T.) Fill a test tube with a saturated solution of chlorine; invert it—mouth under water; place it where direct sunlight may fall upon the tube; examine after a day or two. Results? Test water of tube with litmus paper. Results? If any gas has accumulated in upper portion of tube, test it with a glowing splinter. Results? What are your conclusions as to reaction? Equation?

4. Optional. Introduce into a bottle of chlorine a piece of metallic sodium heated gently in a dephlegrating spoon. Result? Equation?

Experiment III. Optional Methods for Preparation of Chlorine. (Oxidation Processes.)

(*a*) Use equal parts by weight of NaCl and MnO_2; add strong sulphuric acid.

$$MnO_2 + NaCl + H_2SO_4 \rightarrow MnSO_4 + Na_2SO_4 + 2H_2O + 2\overline{Cl}.$$

For stages of reaction (Instruction).

(*b*) Potassium permanganate, with hydrochloric acid added slowly from a "dropping" funnel.

$$KMnO_4 + 8HCl \rightarrow KCl + MnCl_2 + 4H_2O + 5\overline{Cl}.$$

(*c*) To a few crystals of potassium chlorate, add concentrated hydrochloric acid. (This is a convenient and efficient method for preparing small quantities of the gas. It is frequently resorted to by analytical chemists.) The reaction may be represented by the following equation:

$$2KClO_3 + 4HCl \rightarrow 2KCl + \overline{Cl_2O_4} + 2H_2O + 2\overline{Cl}.$$

It must be evident to the student that chlorine possesses considerable chemical energy, and that it manifests a remarkable affinity for hydrogen —the majority of the foregoing phenomena being explained by this fact. Its bleaching properties in the presence of moisture appear to be due to the reaction whereby the hydrogen is withdrawn from the water, liberating *nascent* oxygen which oxidizes the coloring compounds, thus forming new substances which are colorless. Chlorine has frequently been called an "oxidizer" on account of this type of reaction. Frequently compounds are "broken up," i.e., suffer decomposition because of the withdrawal of hydrogen by chlorine.

That which is of dominant interest to us at this time is the compound which is formed as the result of the combination of hydrogen and chlorine, and which in the light of former rules of nomenclature, might be termed *hydrogen chloride.* The properties of this latter substance resembled those of *hydrochloric acid.* This leads us to a study of a class of compounds called "*acids.*"

ACIDS.

In the study of the element chlorine which is a typical *non-metal,* a compound containing chlorine and hydrogen was prepared, which in a number of its properties resembled a class of compounds called *acids.* The investigation of the properties of this compound may warrant the making of certain generalizations which will be of service to us.

Experiment I (L.T.).—Electrolysis or Analysis of Hydrochloric Acid.

Fill a Hoffman V-tube for the electrolysis of hydrochloric acid with a dilute solution of the shelf reagent. Connect the positive pole of the battery with the end of the V-tube which is not ordinarily sealed, but is closed with a cork through which a platinum electrode passes. Pass the current; hold a piece of "test paper" near the open end of tube for three or four minutes. Results? Conclusions?

Test the gas collecting in the other arm of the tube by bringing a lighted match near it. Results? Identity of gas? What are your conclusions as to the composition of hydrochloric acid? Is your view supported by any of the experiments performed with chlorine? Explain. At which electrode was free chlorine (non-metal) liberated? This is a characteristic of non-metals.

Experiment II.—Volumetric Composition of Hydrochloric Acid.

(*a*) Fill the Hoffman apparatus which was used for the electrolysis of water, with a solution of hydrochloric acid. Pass the current for fifteen or twenty minutes simply to saturate the water with hydrogen and chlorine gases, as the latter is particularly soluble; open stop cocks, forcing out the gases; now proceed with the electrolysis to determine the ratio of the combining volumes of hydrogen and chlorine. Recalling Avogadro's rule, what would you say in regard to the relative number of atoms of each gas in a molecule of the acid?

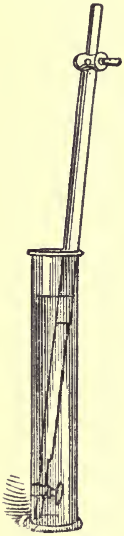
FIG. 24.

(*b*) Optional. Relative volumes of hydrogen and chlorine in hydrogen chloride.

Generate hydrogen chloride as suggested in above experiments, then dry gas by bubbling it through a wash bottle filled with sulphuric acid, or generate it by allowing concentrated sulphuric acid to drop slowly from a separatory funnel into a flask containing concentrated hydrochloric acid. Fill a colorimetric tube or eudiometer (Fig. 24) with the dry gas. Introduce about 10 grams of sodium amalgam and quickly cork the open end. Raise and lower either end of the tube so that the amalgam may come into contact with all portions of the gas. Uncork the tube under mercury. Result? Adjust, so that liquid on outside and inside of tube are at same level. What is the volume? Place thumb over open end of tube and lift it from the liquid; invert; remove thumb and apply a lighted match. Results? What gas was it?

What are your conclusions as to the relative volumes of the two constituents of hydrogen chloride? As to the volume of either constituent relative to the total volume?

Experiment III.—Preparation and Properties of Hydrogen Chloride Gas.

(*a*) Place a small quantity of ammonium chloride in a test tube; add a few drops of concentrated sulphuric acid; hold a piece of blue litmus near mouth of tube. Results? Repeat with red litmus paper. Results? Blow your breath across mouth of tube. Results? Pour a few cm.^{3} of ammonium hydroxide into a test tube, then bring its mouth near to mouth of tube in which gas is being generated. Results?

$$2NH_4Cl + \underset{\substack{\text{1 mol. grm. wt.} \\ \text{2 mol. grm. wts.}}}{H_2SO_4} \rightarrow (NH_4)_2SO_4 + \underset{\substack{\text{2 mol. grm. wts.} \\ \text{1 mol. grm. wt.}}}{2HCl}.$$

To what class of chemical reactions does the above reaction belong?

Write equation for the reaction that occurred when the two test tubes with contents were brought close together.

Experiment IV.—Study of the Properties of the Gas Evolved from Hydrochloric Acid.

Now half fill a test tube with the shelf reagent known as "hydrochloric acid." Using this, repeat the above experiment in its various parts, and record results.

Does there seem to be any similarity in the properties of hydrogen chloride gas and the gas evolved from hydrochloric acid?

Experiment V.—Laboratory Method for Preparation of Hydrogen Chloride Gas.

Arrange apparatus as you did for the preparation of chlorine with this exception, that you raise the tube of the wash bottle which ordinarily dips into the washing fluid (water in this experiment) so that its lower end just escapes the surface of the water. Pour 15 cm.^{3} of water into a beaker; add slowly and while constantly stirring 35 cm.^{3} of concentrated sulphuric acid; let the mixture cool. Introduce 35 grams of sodium chloride into generating flask and observe that all parts of system of apparatus are properly arranged. Place upon the desk a few dry bottles, and a label cut into narrow strips about a cm. long. Set a dry bottle under delivery tube of wash bottle to collect gas by vertical displacement of air. Add slowly through funnel tube about one-half of cooled mixture of water and acid,—if necessary add all of it, and heat gently. Fill three bottles with the hydrogen chloride gas. Half fill a clean test tube with distilled water; mark its height by means of a piece of label; permit the gas to bubble into water in tube until it is saturated; this test tube should be placed in a bath which is at a temperature as near 0° C. as can conveniently be arranged; at least, place tube in a bottle filled with cold water. While waiting for water to become saturated, proceed with following experiments. The above reaction may be represented as follows:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + \overline{HCl}.$$
$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + \overline{HCl}.$$

Experiment VI.—Solubility of Hydrogen Chloride Gas.

Invert one of the bottles of gas over a pneumatic trough, with its mouth under water. Results? Conclusions? Proofs?

Experiment VII.—Density of Hydrogen Chloride Gas.

Using another bottle of the gas, devise a method which will prove approximately that the gas is heavier than air. Can gas be "poured?"

Experiment VIII.—Properties of Hydrogen Chloride Gas in Solution and Hydrochloric Acid.

Before proceeding with this experiment, take up Exp. IX. Divide the aqueous solution of the gas into three equal parts.

(*a*) To one part in a test tube add a piece of granulated zinc. Results? Hold a lighted match near the mouth of the test tube. Result? Conclusions? Repeat this, and all of the following experiments, by using hydrochloric acid from the shelf. Results?

(*b*) To the second part of the solution add a little sodium carbonate. Results?

(*c*) Divide the third part into four portions and dilute each with twice its volume of water. To one of the portions add a few drops of silver nitrate. Result? To another portion add a few drops of mercurous nitrate. Results? To the third portion add lead nitrate. Results? Divide the fourth portion into two parts. To one part add sodium hydroxide. Results?

To the second part add three times its volume of water. Taste it by placing a drop or two on the tongue by means of stirring rod. Does it possess a caustic, lye-like, or an acid, sour taste?

Dip pieces of blue and red litmus paper into the solution. Results? What are your conclusions as to the relation between hydrogen chloride gas in aqueous solution and the shelf reagent, hydrochloric acid?

Experiment IX.—(Quant.) Optional. Density of a Solution of Hydrogen Chloride Gas (Hydrochloric Acid).

When liquid in above test tube (Exp. V) is apparently saturated with gas, remove it and note volume of contents. Results? Now carefully remove all traces of label and wipe dry outside and inside of tube above solution; weigh tube and contents. Record weight; mark height of solution with label; pour contents of tube into another tube to be reserved for preceding experiment; wash tube and fill with distilled water to top of "label;" remove label and wipe tube as before; weigh empty tube when clean and dry. Weight? Find density of solution. Record all calculations.

Experiment X.—General Properties of Acids.

Make very dilute solutions of the following acids, nitric, sulphuric, and acetic. Taste a drop of each. Test them with both blue and red litmus paper. Place a piece of granulated zinc in a dilute solution of each. Test each acid with a solution of sodium carbonate. Make a record of all observations. Do all of the acids have some properties in common? Write the formulæ for hydrochloric, nitric, sulphuric, and acetic acids. What element is possessed in common by all acids? Would you suspect a causal relation between the element and the properties possessed in common by acids?

Experiment XI.—Each Acid Has Characteristic Properties.

Procure from side shelf reagents 4 or 5 $cm.^3$ of lead nitrate in a test tube, and an equal volume of barium chloride in another tube. Divide the lead nitrate into two parts. To one part add a few drops of dilute hydrochloric acid; to the other add dilute nitric acid. Record results.

Repeat the above using nitric acid and sulphuric acid and the barium chloride solution. Record results. Would you say that each acid possesses properties peculiar to itself in addition to its general *acid* properties?

Write equations for all reactions, underscoring the substance which separated out in the solid form (precipitate). Is the precipitate in equilibrium with molecules in solution?

It is difficult to accurately define an *acid* at this stage of our work. From the foregoing experiments it may be deduced that acids are compounds which may be either solids, liquids, or gases. They possess the power to alter certain vegetable colors, namely, to turn blue litmus red; to act upon metals, which displace hydrogen; they have a sour taste and usually contain a non-metal (an electro-negative element) united with hydrogen or hydrogen and oxygen. It is generally conceded that it is the replacable hydrogen of these compounds when in aqueous solution which give them their general *acid* properties.

ACIDS,	Hydrascids.	(HCl, H_2S).
	Oxascids.	($HClO_3, H_2SO_4$).
ACIDS,	Organic.	($HC_2H_3O_2$, $H_2C_4H_4O_6$).
	Inorganic.	(HNO_3, H_3PO_4).

Oxascids are sometimes looked upon as non-metallic oxides combined with water. The oxide is called the *anhydride* ($H_2O.SO_3, H_2O.N_2O_5$).

The part of an acid formula which remains after the hydrogen is removed is sometimes spoken of as the *acid radical.*

OXASCIDS,	Hypo-ous.	($HClO$).
	-ous.	($HClO_2$).
	-ic.	($HClO_3$).
	per-ic.	($HClO_4$).

The above nomenclature is a type of that which is resorted to in order to distinguish between a number of compounds closely related in composition. The endings indicate the relative degrees of oxidation.

Binary Compounds are those which are composed of two elements, M_2O. The names of such substances end in *ide.* This rule relative to nomenclature has preference over any other rule. Ternary Compounds are those composed of three elements, as, H_2SO_4.

SODIUM.

Symbol, Na. At. Wt. 23.05.

Sodium is a typical *metal.* In dividing the elementary substances into *metals* and *non-metals,* it should be remembered, and as we shall see later, the line of demarcation is nowhere distinctly drawn. Midway between these proposed classes there are such elements as arsenic, antimony and bismuth, whose chemical and physical properties permit, under varying conditions, a classification with either the *metals* or *non-metals*. These elementary substances occupying intermediate ground are sometimes called *metalloids*. It is better to regard the elements as constituting a series with a regular gradation of properties.

Sir Humphry Davy succeeded in preparing small quantities of sodium by electrolysis of fused sodium hydroxide, about 1807.

Experiment I.—Properties of Sodium.

(Metallic sodium is usually kept under kerosene. It should always be handled by means of dry forceps.)

(*a*) Place a piece of sodium upon a dry paper and cut off a piece the size of a small pea. Is the sodium hard? Observe the color, luster, and the effect of air. Half fill the pneumatic trough with water which does not turn red litmus paper to blue. Drop the small piece of metal upon the water and step back from the trough. Does the metal float? Is there evidence of chemical action taking place? Fasten a match to a rod; light match, and apply flame to piece of metal. Is there evidence of a flame around the sodium? A flame implies the existence of a gas. Where does the gas come from?

(*b*) Wrap a piece of sodium in a little paper; place it in a wire gauze basket; hold it under water and collect the gas which escapes in a test tube by displacement of water; apply a lighted match to mouth of tube. Results? What gas? The sodium has apparently displaced what from the molecule of water?

(*c*) Test the water in the trough with red litmus paper. Result? Take a little of the water between the fingers.

Pour 3 $cm.^3$ of the shelf reagent labeled sodium hydroxide into a test tube and dilute with an equal volume of water. Repeat above tests. Would you say that they are identical substances? If so how much of the hydrogen was displaced from the molecule of water? Write equation to represent the reaction of sodium and water. What is the valency of sodium?

(*d*) Recall the Exp. in which metallic sodium was introduced into chlorine. Write equation.

(*e*) Flame color of sodium compounds. Dip a platinum wire into a little hydrochloric acid; hold it in flame until it imparts no color to the latter; dip wire into a little sodium hydroxide and hold wire in flame. Is the flame colored? What is the color? Repeat all of above operations using the water of the pneumatic trough. Results? Conclusions?

Sodium is a silver-white metal; it loses its metallic lustre on exposure to damp air due to the fact that under such conditions it readily oxidizes; it is quite soft at laboratory temperatures, but hard at —20° C.; melting point, 96.5° C.; specific gravity, .97; conductor of heat and electricity; is an electro-positive element, separating out at negative electrode, but immediately reacts on the water forming a compound known as sodium hydroxide and liberating hydrogen instead; it possesses relatively a great amount of chemical energy, combining so readily with substances that it is not found in the *free* state in nature. We have seen it displace an hydrogen atom from the molecule of water and combine with the hydroxyl (OH), yielding a compound known generically as a *base* or an *alkali*, and specifically, as *sodium hydroxide* or *sodium hydrate*, which has the property of turning red litmus paper blue.

BASES.

Experiment I.—General Properties of Bases.

Place 3 $cm.^3$ of each of the following in different test tubes, and dilute each with four times its volume of water:—sodium hydroxide, potassium hydroxide, ammonium hydroxide and calcium hydroxide. Test each by means of red and blue litmus paper, tasting a drop, and by taking a little between the fingers. Tabulate data. What are your conclusions as to their similarity with respect to the properties of changing red litmus to blue litmus, alkaline taste (alkalinity, causticity), and lye-like or soapy feeling to touch?

Write the formula of each. Is the hydroxyl common to all? Would you infer a causal relation between properties in common and constituents in common? Ask the instructor to show solid NaOH and KOH, to you.

Experiment II.—Each Base Has Characteristic Properties.

To a few $cm.^3$ of lead nitrate solution add a few $cm.^3$ of dilute hydrochloric acid. Divide the precipitate into two parts. To one part add considerable NaOH (reagent). Result? To the other portion, add NH_4OH in excess. Result?

Using a solution of silver nitrate repeat above experiments. Results? Write equations for above reactions.

As the result of the combination of sodium and the hydroxyl (OH) we have a compound which is typical of a large group of compounds which are known collectively as *bases*. They seem to possess properties which are the very opposite of those possessed by acids. Bases have the power to change red litmus to blue; they have an *alkaline* or *bitter* taste and feel *soapy* to the touch. The term *base* has been very loosely, and frequently, inaccurately applied. It is now usually restricted to the *hydroxides* or *hydrates* of the metals. It seems to be quite well established that the basic or alkaline properties of the bases in aqueous solution, are due to the action of the hydroxyl. Our concept of a base, in regard to its constituents is, that it is a metallic element (metal) combined with one or more hydroxyls, the number depending on the valency of the metal. As would be expected the above enumerated properties are possessed in varying degrees of intensity by the different bases.

Strong bases, like sodium hydroxide and potassium hydroxide, are frequently called *alkalies.* Again, sodium hydroxide and potassium hydroxide are respectively, spoken of, as *caustic soda* and *caustic potash*

	Vegetable.		Fixed.
Alkalies		Alkalies	
	Mineral.		Volatile.

The bases are commonly distinguished from one another by using the name of the metal before the word hydroxide.

Bases are not infrequently considered as being composed of a metallic oxide and water. The oxide is called a *basic oxide.* $BaO + H_2O \rightarrow Ba\,(OH)_2$.

The question might logically be raised at this time, what will occur if an acid and a base (their properties are the opposite of one another) are brought together?

NEUTRALIZATION—SALTS.

Experiment I.—Electrolysis of a Salt.

Make a strong solution of sodium sulphate. Test the solution with both red and blue litmus paper. Is the solution neutral? Place solution in U-tube for electrolysis after having added a sufficient quantity of litmus solution to give a decided blue color to the entire volume of liquid. What changes of color occur when current is passed? What is liberated at either pole? Write equations to represent all reactions.

Experiment II.—A Quantitative Study of the Interaction of Acids and Bases.

Assemble two burettes (Fig. 25) and clean them thoroughly. Clamp them into proper position. Fill the burette at your right with dilute hydrochloric acid (1 of acid to 20 of water). Fill the left burette with a dilute solution of sodium hydroxide (1 part of shelf reagent to 10 of water). Run out acid and alkali so that both burettes give zero reading. Clean a small Erlenmeyer flask; place a piece of white paper under either burette. Place flask under "acid" burette and run into it 9 $cm.^3$ of acid. Be sure to read from the lower side of meniscus. Add a few drops of litmus solution or a small piece of red litmus paper. Now place flask under "alkali" burette and introduce cautiously enough of the alkali to just turn the litmus color to a permanent blue. From time to time shake the flask vigorously to bring alkali and acid into intimate contact, or stir with a glass rod, but don't take the rod out of the flask. Draw from the burettes alternately as is necessary to bring the solution to the point when a drop of either will cause a change in color. When this point has been reached the solution is *neutral.* Record the number of $cm.^3$ of each used. The process is known as *neutralization.* Taste the solution. Place 15 or 20 $cm.^3$ in an evaporating dish and evaporate to dryness. Taste the *salt.* Has it a familiar taste? While waiting for the solution to evaporate, repeat first part of operation by finding how many $cm.^3$ of the alkali will be required to neutralize 15 cm.^{3} of acid; then repeat again, using 12 cm.^{3} of acid. Tabulate all data.

Does the Law of Definite Proportions receive a verification by your results?

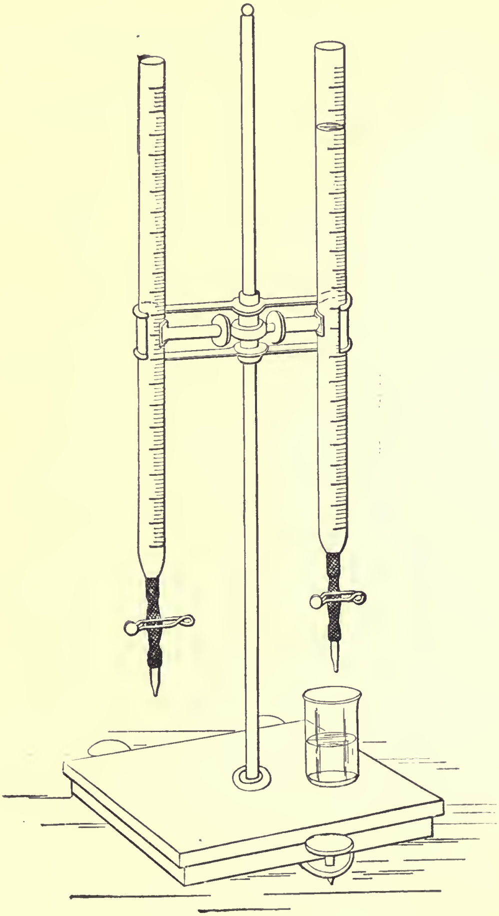

FIG. 25.

If time permits, other acids and bases may be used and their ratios determined. Write equations.

What do you have in the acid that you do not have in the neutral salt? Answer the same question in regard to the alkali. What has become of these two substances? Is it possible that their removal from the neutral substances is in any way related to the property of "neutrality?"

Write the equations representing the respective reactions of H_2SO_4, HCl, and HNO_3 with KOH, NH_4OH, and $Ca(OH)_2$.

Experiment III.—Interaction of a Metallic Oxide and an Acid.

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O.$$

Experiment IV.—Interaction of Metals and Acids.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + \overline{H_2}.$$

Experiment V.—Action of an Hydroxide as a Base and as an Acid.

To a few cm.³ of Pb $(NO_3)_2$ add a few cm.³ of NaOH. Note the precipitate. Filter. Divide the precipitate into two parts. To one part add HNO_3; to the other, add an excess of NaOH. Is there any similarity in the action of the acid and the base in these latter reactions? Write equations.

Experiment VI.—Action of a Base on a Salt.

To 3 cm.³ of Fe SO_4 add a few cm.³ of NH_4OH. Results? Equation?

Experiment VII.—Action of an Acidic Oxide upon a Base.

$$CO_2 + Ca\,(OH)_2 \rightarrow \underline{CaCO_3} + H_2O.$$

Experiment VIII.—Interaction of Salts.

$$HgNO_3 + Na\ \ Cl \rightarrow \underline{HgCl} + NaNO_3.$$

Experiment IX.—Preparation of a Basic Salt.

Recall the experiment in which $BiCl_3$ which is soluble, was changed into an insoluble basic salt by hydrolysis. Define Hydrolysis.

$$\begin{array}{l}
\quad H_2O \rightarrow H^{\cdot} + OH' \\
BiCl_3 + 2H^{\cdot} + 2OH' \rightleftarrows \underline{Bi(OH)_2Cl} + 2HCl \\
\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\
\qquad\qquad\qquad\qquad \underline{BiOCl} + H_2O.
\end{array}$$

Experiment X.—Preparation of an Acidic Salt.

Fill a burette with NaOH as found in the reagent bottles. Fill another burette with a cold solution of H_2SO_4 (1 of acid to 2 of H_2O). Neutralize 5 cm.³ of acid with NaOH. Record number of cm.³ used. Evaporate solution until it becomes saturated. Crystals will separate out when it becomes cold. To the same volume of NaOH as used above, add twice the quantity of H_2SO_4 necessary to neutralize it. Proceed as above. It may be necessary to let solutions stand a couple of days before crystals appear. Compare crystals as to appearance, water of hydration, and reaction toward litmus. Write equations.

Experiment XI.—Classification of Salts.

Under the heads of Normal, Acidic, and Basic, arrange the following salts with reference to their action toward litmus paper. A few cm.³

of a solution of each will be sufficient. Write formula for each salt. Sodium chloride, sodium hydrogen sulphate, copper sulphate, aluminum chloride, sodium hydrogen carbonate, sodium carbonate and potassium sulphate.

A *salt* is the chief product of the interaction of an acid and a base, or (a) it is an acid in which the hydrogen, wholly or in part, has been replaced by a metal, or (b) it is a base in which the hydroxyl has been replaced wholly or in part by the acid radical. Both (a) and (b) are necessary to cover all cases.

This interaction of acids and bases is a species of reaction known as *neutralization*. It may be considered as a process in which the removal from solution of the hydrogen and hydroxyls is effected, wholly or in part, by arranging the conditions favorable to their combining and forming neutral water. A more specific detailed definition may be offered later. Neutralization is a quantitative process.

Would you expect a definite thermal conduct when given quantities of hydrogen and hydroxyls combine to form molecules of water?

Thermo-chemistry of neutralization.—

$$NaOH + HCl \rightarrow NaCl + H_2O + 137000 \text{ cal.}$$
$$KOH + HNO_3 \rightarrow KNO_3 + H_2O + 137000 \text{ cal.}$$
$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + (2 \times 137000) \text{ cal.}$$

The heat liberated during the process of neutralization is called the "heat of neutralization."

		Acid Salts.
	Partial,	
		Basic Salts.
Neutralization,		
	Complete,	Normal Salts.

An *acid* is a substance containing hydrogen which may be replaced wholly or in part by a metal.

A *base* is a substance containing hydroxyls which, ordinarily, may be displaced wholly or in part by the acid radical.

In the preceding experiment we have seen that bases sometimes conduct themselves like acids.

$$Pb(OH)_2 + 2Na\,OH \rightarrow Na_2Pb\,O_2 + 2H_2O.$$

As we proceed it will become evident that narrow rigid classifications are not always possible.

	Mono-basic, (HCl),		Mon-acid, (NaOH),
Basicity,	Di-basic, (H_2SO_4),	Acidity,	Di-acid, $Ca(OH)_2$,
	Tri-basic, (H_3PO_4).		Tri-acid, $Bi(OH)_3$.

Oxacids ending in *ic* give *ate* salts.
Oxacids ending in *ous* give *ite* salts.
Oxacids with *hypo* and *per* affixes yield corresponding salts.
$HClO$ forms *hypochlorites*,
$HClO_2$ forms *chlorites*,
$HClO_3$ forms *chlorates*,
$HClO_4$ forms *perchlorates.*

A *metal* may now be defined as a base-forming substance. NH_4 is sometimes called a *hypothetical* metal.

A non-metal may be regarded as an acid-forming element. The student should keep clearly in mind the relations between *hydrogen* and *acidic* properties, and *hydroxyls* and *basic* properties.

PROBLEMS.

1.—A liter of a given solution of NaOH contains 40.058 grm. of the solute; an acid solution of unknown strength was titrated against the alkali solution when it was found that 50 $cm.^3$ of the acid solution was required to neutralize 25 $cm.^3$ of the alkali. What was the normality (strength) of the acid solution?

2.—How many grm. of H_2SO_4 will be required to neutralize 1500 $cm.^3$ of a 2 N solution of KOH? To neutralize 400 $cm.^3$ of a 5 N solution of $Ba(OH)_2$?

3.—If 500 grm. of $Na_2SO_4.10H_2O$ are prepared by neutralization, how many grm. of acid were required? Of alkali?

4.—If you were asked to determine the strength of an acid solution, how would you proceed, assuming that you have access to a well equipped laboratory?

5.—Define Alkalimetry. Acidimetry. Titer. Titration.

CHAPTER XIII.

CHEMICAL EQUILIBRIUM, REVERSIBLE REACTIONS, MASS LAW, DISSOCIATION.

"A chemical change in a given system is said to be *complete* when it proceeds continuously with increase of 'products' and a corresponding decrease of 'factors,' until one or more of the factors is exhausted and the reaction ceases for want of more material. When increase in quantity of products and decrease in the quantity of factors are arrested before one or more of the factors is exhausted, it is known as an *incomplete chemical change.*"—Ostwald.

In the union of hydrogen and oxygen at various temperatures, to form water, it will be recalled, that if the mixture of gases (2 vols. of H to 1 vol. of O) was "sparked" at the ordinary temperature of the laboratory the reaction continued with great speed until all the factors had been exhausted, i.e., the reaction ran to an end. It will also be remembered that if this quantity of water be heated to a temperature of 2500–3000° C., it dissociates slightly into H and O gases. $2H_2O \rightarrow 2H_2 + O_2$. Now it is further known, that in a *closed system* composed of H_2O (steam) at 3000° C. and H and O gases formed as the result of the decomposing influence of heat, if the temperature is lowered the H and O tend to recombine and form H_2O, that is, the reaction runs to the left as shown by the equation (1); if the temperature is again raised then equation (2) represents the nature of the reaction.

$$
\begin{aligned}
&(1)\ 2H_2O \leftarrow 2H_2 + O.\\
&(2)\ 2H_2O \rightarrow 2H_2 + O.\\
&(3)\ 2H_2O \rightleftarrows 2H_2 + O.
\end{aligned}
$$

It is evident that the H and O gases are in *equilibrium* with water (steam), and the reaction is *reversible.* (Decompositions which are reversible are called *dissociations.*) Increase of temperature tends to produce a greater degree of dissociation; lowering the temperature tends to produce a greater degree of association. What will be the effect of increasing the pressure on the system? Assuming that definite volumes of H and O gases are in equilibrium with the steam, apply pressure or introduce into the system volumes of either gas or both, then equation (1) will represent the resulting reaction; if the pressure is diminished or a portion of either gas, or both, is removed, equation (2) shows the direction of the reaction.

A more detailed explanation may make the above phenomena more easy of interpretation. Conceive of the steam at 3000° C. being placed in a cylinder which has a movable piston and a stop cock. Keep the temperature constant and diminish the pressure on the components by pulling the piston well out toward the end, the steam will dissociate in part into definite volumes of H and O—always the same quantities under identical conditions. Inside of the cylinder there is a definite concentration of each substance. The concentrations of the H and O gases are very small, but not so small but that these particles meet one another every now and then, and uniting, form water, but this immediately diminishes the pressure on the remaining components of the system for *three volumes* (2 of H and 1 of O) of hydrogen and oxygen gases combine to form only *two* volumes of steam. Owing to this diminished pressure more steam dissociates and the equilibrium is reestablished. Now introduce through stop cock some H gas, this increases the pressure upon the system, but especially does it increase the concentration of the H particles, with the result that they meet the O particles more frequently, and combination to form water is more rapid than under original conditions. In other words, the speed of the reaction as shown by (1) is much greater than the speed of the reaction indicated by (2), but after the reaction (1) has continued for some time its speed will become less owing to diminished concentration of the hydrogen particles. Oxygen gas introduced, would have yielded similar results. Any factor which alters the concentration of the "factors" or "products" will alter the general direction of the reaction. If either of the components of the system had been removed, the effect upon the nature of the ensuing reaction would have been just as marked, only the reaction would have proceeded as indicated by (2).

The above is one of many examples of *concentration effect* or *effect of mass* upon chemical reaction. So important is the influence of "active mass" upon chemical reaction that it has been stated in the form of a law by Guldberg and Waage. It is known as the Mass Law.*

"*Interactions of substances depend not only upon the affinities involved, but also upon the active mass of the substances in a unit volume.*"

$$2H_2O \rightleftarrows 2H_2 + O_2.$$

$$C_1^2 = C_2^2 + C_3.$$

$$K = \frac{C_2^2 . C_3}{C_1^2}$$

K is sometimes called the *affinity constant.* It really represents the ratio of the affinities urging the opposed actions. The speed of the reaction represented by (1) may be indicated by $\text{Speed}_1 = K_1 C_1^2$ and the opposed reaction by $\text{Speed}_2 = K_2 C_2^2 . C_3$ where K_1 represents the

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*Professor T. W. Richards prefers to call it, "The Law of Concentration Effect.

tendency for water to dissociate, and K_2 the tendency for H and O to combine.

$$K_1C_1^2 = K_2C_2^2.C_3; \quad \frac{K_1}{K_2} = \frac{C_2^2.C_3}{C_1^2}; \quad K = \frac{C_2^2.C_3}{C_1^2}.$$

Experiment I.—Reactions which are Approximately Complete.

(*a*) Formation of an inactive and practically insoluble product. Pour 3 cm.^{3} or 4 cm.^{3} of silver nitrate ($AgNO_3$) solution into a test tube, (use side-shelf reagent); add a few drops of a dilute solution of sodium chloride (NaCl); let the precipitate curd and settle to the bottom; observe whether an increase in the quantity of the precipitant will cause additional precipitation. Continue to add the precipitant until subsequent additions do not effect further precipitation of silver chloride (AgCl). Equation? Are the "products" of the reaction, active or inactive? Explain. Is it possible that under certain conditions the "products" may react to produce the "factors?" Are all substances soluble in degree? Is the precipitate (AgCl) in equilibrium with the small quantity which is dissolved?

(*b*) Formation of a product (gaseous) which is removed. Prepare a dilute solution of sodium carbonate (Na_2CO_3); test with litmus solution; add a few drops of dilute sulphuric acid (H_2SO_4) at a time and note effect upon the speed of the reaction; continue to add acid until the effervescence of CO_2 has ceased, and blue litmus begins to turn red. Equation? When one of the products escape from the system, is it likely that the "products" will react to produce the so-called "factors?" Is there any likelihood of the establishment of an equilibrium between the "factors" and the "products?" If not, is the reaction reversible? Explain.

Experiment II.—Reactions which are Incomplete. Equilibrium.

(*a*) Reversible reaction. To 5 cm.^{3} of a magnesium sulphate or chloride solution (side-shelf), add a few drops of NH_4OH at a time: observe the *partial* precipitation of magnesium hydroxide ($Mg(OH)_2$); now add an excess of NH_4OH and note that subsequent additions of NH_4OH do not effect further precipitation.

$$(1)\ MgCl_2 + 2NH_4OH \rightleftarrows \underline{Mg(OH)_2} + 2NH_4Cl.$$

Now add an excess of ammonium chloride, NH_4Cl—one of the "products," and observe that the presence of a large concentration of this "active mass" causes reversal of reaction as indicated by (1).

$$Mg(OH)_2 + NH_4Cl\ (excess) \rightarrow MgCl_2.2NH_4Cl + NH_4OH$$
$$MgCl_2 + NH_4OH + NH_4Cl\ (excess) \rightarrow MgCl_2.2NH_4Cl + NH_4OH.$$

Inasmuch as $Mg(OH)_2$ is soluble in NH_4Cl which is formed simultaneously, would you say that there is a complete precipitation in the first reaction? Do the "products" tend to react and reproduce the "factors?" When the speeds of these opposing reactions are the same, a condition of *equilibrium* results. Was the speed of the reverse reaction increased by increasing the concentration of one of the "active products"? If the NH_4Cl is removed as rapidly as it is formed in first reaction, will the reaction be complete? Will there ensue a condition of equilibrium? Will the reaction be reversible?

(*b*) An incomplete reaction completed by rendering one of the active products inactive by virtue of its insolubility in another medium. To 15 cm.^{3} of a dilute solution of calcium chloride, $CaCl_2$, add a few cm.^{3} of a concentrated solution of potassium sulphate, K_2SO_4; observe the slight and partial precipitation of calcium sulphate, $CaSO_4$.

$$CaCl_2 + K_2SO_4 \rightleftarrows \underline{CaSO_4} + 2K\ Cl.$$

Filter, and add 5 cm.^{3} of ethyl alcohol, C_2H_5OH, to 5 cm.^{3} of the filtrate. Explain the formation of the heavy precipitate of $CaSO_4$.

(*c*) A reaction involving equilibrium, in which each of the opposing reactions are practically completed by varying the concentration of the "active masses."

Add a few cm.^{3} of an oxalic acid, $H_2C_2O_4$, solution to 5 cm.^{3} of a dilute $CaCl_2$ solution; the precipitation of the calcium oxalate, CaC_2O_4, is incomplete owing to the reaction of HCl which is formed simultaneously.

$$CaCl_2 + H_2C_2O_4 \rightleftarrows \underline{CaC_2O_4} + 2HCl.$$

Decant half of the solution upon a filter, and collect the filtrate. To the portion remaining in the test tube add HCl until precipitate dissolves. Write equation. To the filtrate add two or three cm.^{3} of a sodium acetate, $NaC_2H_3O_2$, solution. Explain formation of precipitate of CaC_2O_4. Write equations. Compare the reactions as represented by equations. Are the reactions as represented by your equations, opposite in nature? If these two opposing reactions should occur in one system, with identical speeds, would a condition of equilibrium results?

Berthollet's Laws are in substance as follows:

"*If the 'products' are not active*, or *are active but are removed, then the reaction is complete and runs to an end.*"

"*When the products of a reaction are chemically active within a system* and *are not removed, the reaction is reversible and incomplete, and results ultimately in balanced action and chemical equilibrium.*"

Chemists are now inclined to regard all chemical changes as being reversible, i.e., reactions do not run to completion.

A thorough understanding of Le Chatelier's Theorem will enable the student to understand much in regard to chemical equilibrium which would otherwise be vague. (See Energetics of Chemistry.)

Before leaving this subject the student is warned against looking upon a condition of chemical equilibrium as being due to a cessation or suspension of chemical action. On the contrary such a state of balance is due to the fact that the speeds of the opposing reactions are equal. Again, a reversible action must not be considered as one which runs to completion, when an opposite reaction is then initiated and runs backward. Both actions are started at practically the same time; the one gradually increases in speed and the other gradually diminishes in speed until finally their speeds are identical, when a condition of equilibrium results.

Experiment III.—Dissociation of a Gas.

Place a small quantity of NH_4Cl in a dry test tube; heat tube until white fumes are evolved and sublime up the tube. Now hold a piece of moistened red litmus paper in the mouth of the tube and it will be turned blue showing that a portion of the ammonia is escaping; discontinue heating tube for a moment and the blue litmus paper will be turned red owing to the hydrogen chloride which is now escaping. Heat tube strongly, and hold litmus paper in the heavy white fumes which appear a few inches above the mouth of the tube. Results? This is a case of *dissociation.* Is temperature a factor in determining which way the reaction shall go? Explain. Would you say the *heat of dissociation* is positive or negative?

$$NH_4Cl \rightleftarrows \overline{NH_3} + \overline{HCl}.$$

Many gases tend to dissociate when placed under favorable energy conditions. At a temperature of

$$\begin{aligned} &2HI \rightleftarrows H_2 + I_2 \\ &N_2O_4 \rightleftarrows NO_2 + NO_2 \\ &I_2 \rightleftarrows I + I \\ &NH_4Cl \rightleftarrows NH_3 + HCl. \end{aligned}$$

480° C. about 20 per cent. of the original quantity of HI is in the dissociated condition.

CHAPTER XIV.

NOTE ON THE MODERN THEORY OF SOLUTION.

The subject of "solutions" was introduced in a preceding chapter, but little was said about the condition of the solute when in solution. Attention was called to the fact that a substance in solution conducts itself very much like a gas, and when the dissolved portion is in equilibrium with an undissolved portion, the solution is said to be saturated. However, the mechanism of a solution was not considered in detail.

The purpose of these notes and the following experiments is to present a comprehensive view of the modern theory of solution.

The theory has grown from the wrecks of other theories. Glimpses of and approximations to the present theory logically preceded it. Therefore, it is somewhat difficult to say just where it had its beginnings; however, it is certainly the result of bringing together, interpreting and correlating a mass of apparently unrelated experimental data.

Without detracting one iota from the man who elaborated the theory in practically its present form, we must acknowledge that we are indebted to other men as well as to Arrhenius for the "Ionic Hypothesis" or The Electrolytic Dissociation Theory.

Although the theory in its present form has been unable to meet in an altogether satisfactory manner all of the requirements made of it, yet it is quite possible when various relationships are more perfectly understood that it will meet all demands. It is so vastly superior in its ability to interpret an array of phenomena which would otherwise be inexplicable that many noted investigators have called the theory "a corner-stone of physical chemistry."

On investigating the labors of the chemists and physicists who preceded and were contemporaneous with Arrhenius, it appears as though it would be perfectly justifiable to affirm that the theory as elaborated was or could have been reached along practically two independent lines of thought and investigation; namely, "electro-chemical" and "osmotic and vapor pressure effects." That as it may or may not be, the literature reveals Arrhenius, himself working along electro-chemical lines, as standing at the apex of two converging lines of investigation; in fact, responsible for causing the lines to meet when they did. It was Arrhenius who elaborated and enunciated the theory which correlated a great volume of isolated data. Other men had been unable to do so. It was Ostwald who then took up the theory, applied it, and finally became its most effective and influential exponent. The theory now meets with an almost universal acceptance.

To use the historical method of approach to our subject—that is, to move historically along the two lines above enumerated—would be perhaps the most satisfactory, but this work is neither so voluminous nor pretentious as to attempt more than to merely mention briefly the names of the men who have contributed to the development of the theory.

Electro-Chemical.—We shall not comment on the labors of Gilbert, Dufay, Becaria, Priestly, Cavendish, Franklin, Wilke, Galvani, Volta and Ritter, J. W., further than to say that Volta originally separated all conductors of electricity into two classes—a *first class*, comprising the metals, carbon and other good conducting substances found in nature, such as metallic sulphides; the *second class* embraced such *solutions* as are conductors of electricity. Until very recently we have spoken of the first class of conductors as those in which when the current is flowing there is no "simultaneous motion of the ponderable matter," while in the case of the *second class* there is supposed to be a "corresponding motion of ponderable matter." That the flow of electricity through conductors of the first class is *convectional*, as well as in the case of conductors of the second class, is a recent theory that is supported by many.

About the year 1800 Nicholson and Carlisle found that when an electric current was passed through two wires whose ends dipped into water, that hydrogen and oxygen gases were liberated, and further, the liquid around the pole at which the hydrogen was evolved was alkaline, while it became acid around the other pole.

In 1802 Ermann secured results very similar to those of Nicholson and Carlisle. Men attempted to explain the acid and alkaline reactions by asserting that it was due to the effect of electricity upon water.

Sir Humphry Davy (1778–1829) investigated the above phenomena and demonstrated that pure water is separated into hydrogen and oxygen gases, and that the acid and alkaline properties were due to impurities in the water. Davy performed the experiment known to us as the "electrolysis of sodium sulphate," the solution having previously been colored blue with a litmus solution. A satisfactory explanation of the phenomena was not offered until many years later. Davy advanced that which may be called the first "electro-chemical theory." It was based upon Dalton's atomic hypothesis. In brief, his theory assumed that the atoms of the elements when they came in contact with one another took to themselves opposite charges of electricity; that if the charges were sufficiently strong the two elements combined, forming a chemical compound. Also, if a new and different atom came in *contact* with the compound and could assume a sufficiently strong charge of electricity, it would attract the oppositely charged atom of the compound, causing decomposition. The theory did not meet with a ready or even an ultimate acceptance.

Berzelius (1779–1848) now advanced his "dualistic theory" which involved the "bipolarity of atoms." Affinity depended upon the size and sign of the dominant electrical charge on the atom. Every compound was conceived of as being composed of two parts, oppositely charged—the parts themselves might be composed of two parts. For example, the salt, $Zn\,SO_4$, should be written according to Berzelius, ZnO.-

SO_3, to show its real structure as being composed of a basic oxide and an acid anhydride. (See Le Blanc's Electro-Chemistry.)

Grotthus (1805) announced the first complete theory of electrolysis, known as the "exchange of partner theory." Clausius showed theory to be a violation of the "second law of energetics." (Lehfeldt's Electro-Chemistry contains a concise statement of the theory.)

Faraday (1794–1868) found that the *quantity* of electricity passing through a circuit and the chemical and magnetic effects produced were proportional to one another. By a series of careful measurements Faraday, in 1833, established the first of two laws known as Faraday's Laws. In substance the First Law is: *the amounts of substances which separate at the electrodes during electrolysis are strictly proportional to the quantity of the electric current which passes through the electrolyte.* The Second law says: *the mass of any substance liberated at the electrodes by a given quantity of electricity is directly proportional to the "chemical equivalent"* or combining weight. Davy believed that the current was carried through solutions by little particles called "ions." He also injected into our nomenclature such terms, as *electrolysis* (the process of decomposing substances in solution by an electric current), *electrolyte* (the substance which carries the current), *anode* (the positive electrode), *cathode* (the negative electrode), *ions* (the particles into which the substance divides and act as the real carriers of the current), *anions* (the ions which gather at the anode), and the *cations* (ions which gather at the cathode).

Note.—The student is reminded that although we shall retain these terms, Faraday did not use them in the sense in which they are used at the present time.

At that time there was considerable discussion as to what constituted the anions and the cations. Berzelius said in the case of sodium sulphate, which he wrote NaO and SO_3, that NaO and SO_3 constituted respectively the cations and anions—that these reacted upon the water and produced an alkali, $NaO + H_2O \rightarrow Na(OH)_2$, and an acid, $SO_3 + H_2O \rightarrow H_2SO_4$, but it was known that hydrogen and oxygen were liberated at the same time.

Daniell disproved Berzelius's explanation by experimentally showing that the hydrogen and oxygen liberated were chemically equivalent to the alkali and acid formed. This would require, so to speak, "double electrical action" which would be contrary to Faraday's laws. Daniell affirmed that Na was the cation and SO_4 the anion; that these ions were set free at the poles, and then reacted upon the water liberating hydrogen and oxygen. "The salt alone must have conducted the electricity in the solution," for if the water had conducted a part of the current of electricity there would not have existed the interequivalence of acid and alkali, and hydrogen and oxygen.

It became known later that both Ohm's law and Joule's law hold for conductors of the second class as well as for the first class, therefore it was obvious that none of the current spent in traversing an electrolyte was employed in doing chemical work in splitting up the electrolyte into ions. *Within* the electrolyte during electrolysis the current merely exerts a *directive force* on the ions; that is, so to speak, "*sorts*" them.

The theory of Grotthus, as mentioned previously, was found to be in conflict with the "second law of energetics" by Clausius, who advanced a theory of his own, in which he set forth the idea that the positive and negative parts of a molecule in a solution are frequently in such a rapid state of vibration that for a few moments at a time the parts may be said to be independent of one another, so that if a current were passing at the time the parts might be so favorably arranged as to follow the directive force of the current and be deposited on electrodes. In other words, he assumed a constant interchange of the negative and positive parts of the molecule, and at any instant there was a small number of these parts of the molecules momentarily free, and that the current was carried by these molecule-parts. This theory was commonly accepted and is the one which preceded our present theory.

Hittorf began his work about this time, on what he called the "migration of the ions." He found during the electrolysis of a $CuSO_4$ solution between electrodes of copper, that the solution became very much more concentrated around the anode then around the cathode, yet the quantity of copper deposited at the cathode was greater than the amount lost by the cathode chamber. The conclusion was not difficult that the ions of Cu and SO_4 had different migration velocities. From the speed ratios Hittorf calculated the "transport numbers."

Kohlrausch, as the result of his work on the conductivity of dilute solutions, established a very simple relation between the "transport numbers" and the *molecular* conductivity. Kohlrausch's work also emphasized the fact that inorganic substances, such as acids, bases and salts, were good conductors (electrolytes), and organic substances were either non-conductors or very poor conductors.

As the result of the labors of Hittorf and Kohlrausch, Svante Arrhenius (1887), a Swedish chemist, was enabled to reach certain conclusions regarding the theory of "free ions." Arrhenius while working on the conductivity of solutions recognized two kinds of "molecules"—one active and the other inactive—as he named them because of the belief that only the "active" molecule was instrumental in causing conductivity. He stated further his belief that the "inactive" changed into "active" molecules with sufficient dilution. He was not able to offer a convincing proof until he was placed in receipt of certain data from the other line of investigation referred to before, namely, "osmotic and vapor pressure" effects.

It had not been so very long before this time that investigators had accepted with considerable hesitancy "the dissociation of molecules" as the explanation of the deviations of many vapor densities from that anticipated by theory. Planck at this time as the result of purely thermodynamical considerations said that "it would be quite natural to expect a similar dissociation when substances were placed in solution."

Osmotic Pressure.—Without attempting to make a complete review of all the work that had been done along this line up to the time of Arrhenius, it will be dismissed with the statement that the question of solution had been holding the attention of eminent investigators for a period of ten to fifteen years preceding the time at which Arrhenius announced his theory. The fundamental idea which stimulated men to these investigations was that when a substance is in the dissolved condition it behaves in a manner very similar to a gas. Although the idea was not new, yet it secured the attention of Van't Hoff (now in the University of Berlin), who became firmly convinced of the fact that a "*substance in solution behaves like a gas and, like it, exerts a pressure*," but he was unable to devise a method for the measurement of the pressure.

We are told that Van't Hoff was one day walking with De Vries, the zoologist, and remarked about the pressure which forces upward the sap in a tree, whereupon De Vries replied that Pfeffer, the botanist, had investigated and also measured the force. This was the very data for which Van't Hoff had been searching.

Pfeffer had observed some years previously that when a plant cell was placed in very dilute solutions it bursted, and when placed in concentrated solutions, the cell shriveled. At the time Pfeffer was unable to make any satisfactory measurements, but later, due to the labors of Traube, he was able to deposit semipermeable membranes of copper-ferrocyanide in the walls of porous porcelain cups which he connected with a manometer; the cup was then filled with a sugar solution and immersed in pure water. As the result of Pfeffer's experiments, although he was unaware of their far-reaching influence, it was found that the pressure (osmotic) was directly proportional to the concentration and the absolute temperature of the solution. Van't Hoff was quick to correlate osmotic pressure and gas pressure. He found, in other words, that the gas laws hold approximately for osmotic pressure. Further, in substance, that equal fractions of the molecular-gram weights of *organic* substances dissolved in the same volume of water produce the same osmotic pressure. To state his conclusions from another point of view and include Avogadro's rule, "*At the same osmotic pressure and temperature equal volumes of all solutions contain the same number of molecules, and, in fact, that number which under the same pressure and at the same temperature exists in the same volume of gas.*" As Van't Hoff proceeded with his work he found that strong inorganic acids and bases and salts did not act normally, i.e.,the osmotic pressures as yielded by solutions of these substances were sometimes more than double that which he anticipated; for example, when a given weight of hydrogen chloride was dissolved in water it gave an osmotic pressure equal to almost twice that which it should yield according to the gas law ($PV=RT$). He was unable to account for this.

Freezing Point and Vapor Pressure of Solvents.—About this time Raoult made two important generalizations in regard to dilute solutions which came as the result of the labors of himself, Bab, Wullner, Ostwald, Blagden, Rüdolph and others. Our knowledge of the depression of the freezing point and elevation of the boiling points of solvents by dissolved substances, was uncertain and fragmentary before Raoult initiated his investigations. (See chapter on "Solutions.")

General Law of the Vapor Pressure of Solvents.—1 *molecule of a non-saline, non-volatile substance, dissolved in* 100 *molecules of any volatile liquid, lowers the vapor pressure of this liquid by a nearly constant fraction of its value—approximately* .0105.

The experience of Van't Hoff relative to osmotic pressures was the experience of Raoult in regard to deviations from his law concerning the freezing point, namely, that *organic* compounds gave normal and comparatively uniform results, while strong *inorganic* acids and bases and salts gave a larger depression than was anticipated. Raoult was likewise unable to explain it.

In the year 1887 Van't Hoff contributed an article to the Zeitschrift für physikalische Chemie on "The Role of Osmotic Pressure in the Analogy Between Solutions and Gases." The article was in support of his belief that the gas law was applicable to dilute solutions of substances. It called attention to the work of Rauolt and emphasized the fact that the use of strong acids and bases caused deviations from both his own and Raoult's laws. Near the latter end of the article Van't Hoff says, "* * * Arrhenius pointed out to me, by letter, the probability that salts and analogous substances when in solution break down into ions. As a matter of fact, as far as investigation has been carried, the solutions which obey the law of Avogadro are non-conductors, which indicates that they are not broken down into ions; and a further experimental examination of other solutions is possible, since, from the assumption made by Arrhenius, the deviation from Avogadro's law can be calculated from the conductivity."

As soon as the above article appeared, Arrhenius was able, by comparing the effects of electrolytes and non-electrolytes in depression of the freezing point of water with their respective electrical conductivities, to produce convincing proof of his original assumption of the electrolytic dissociation of certain salts in aqueous solution. The organic compounds of Van't Hoff and Raoult were the non-electrolytes of Kohlrausch and Arrhenius.

Arrhenius set forth his proof and theory in an article entitled, "Uber die Dissociation der im Wasser gelösten Stoffe." He called attention to the fact that the compounds, salts, strong acids and strong bases which create abnormally high osmotic pressures and abnormal depressions of the freezing point are all electrolytes—i. e., when dissolved in water their solutions become good conductors of electricity; on the other hand, the substances which give normal osmotic pressures and normal depressions of the freezing points are either non-electrolytes or conduct the current very poorly. A normal solution of cane sugar, which is a non-electrolyte, freezes at —1.87° C.; a normal solution of sodium chloride which is a good electrolyte freezes at —3.46° C. A very similar relation holds in regard to the osmotic pressures of the two solutions. It is generally accepted that the pressure of a gas or the osmotic pressure or the depression of the freezing point is directly proportional to the number of molecules or ultimate particles present in the gas or solution. Arrhenius concluded, therefore, that if electrolytes produced abnormal alterations in these particular properties, that the molecules of the substance in solution split up (dissociated) into a larger number of particles which, so far as above phenomena are concerned, acted like molecules. Each of these particles would produce its own effect on osmotic pressure or depression of the freezing point and that inasmuch as those substances which behaved normally with reference to osmotic pressure, etc., were non-electrolytes, these smaller particles were the real cause of the conductivity of a solution. Arrhenius gave the general name *ions* to these independent particles into which molecules were assumed to dissociate. The terminology of the theory is very similar to that suggested by Faraday; in fact, many parts are identical.

Theory.—In briefest outline, his theory is as follows: Whenever an electrolyte, referring to the solute, is dissolved it almost wholly or partly dissociates into ions. The extent of the dissociation depends upon nature of soute, concentration, solvent, temperature and pressure. These ions many be composed of one or more atoms, but are altogether different in nature from the elementary substances of which they are composed. These ions are electrically charged, whereas the elementary substances are neutral, therefore their energy content is different, and logically we expect a difference in properties. An electrolyte dissociates into two ions—one (cation), bearing a positive, and the other (anion), a negative charge of electricity. Frequently one of the ions further dissociates or it may associate with another ion forming a complex ion. It should be remembered that the solution as a whole is electrically neutral and therefore, there must be as many electrical charges of one kind as there are of another. Irrespective of the masses of the ions, the number of charges carried by each ion is equal to the valency of the atom or atomic group which constitutes the ion. As a matter of fact, on the electrical theory, *valency* really amounts to nothing more or less than the "*number of positive or negative unit charges associated with the chemical atom.*" An example may make the theory more easily understood. When hydrogen chloride is dissolved in water it immediately dissociates into ions of hydrogen (hydrion) and chlorine (chloridion), respectively known as cations and anions. The ions are wholly independent of one another. Each ion retains its identity, i.e., properties of reaction, velocity, etc., regardless of its birth. Dilution increases the extent of the dissociation. If the solution is examined, there will be no evidence of any free atoms of either hydrogen or chlorine gas. If these gases were in the free state they would be very easy to detect as hydrogen is very slightly soluble and chlorine is a yellow colored gas. The fact that no electrical energy is consumed in dissociating the molecule *within* the liquid, and yet when a current is passed through the solution the hydrogen ions (cations) are directed toward, and will appear, at the negative electrode (cathode), while the chlorine ion (anion) is attracted to the positive electrode (anode), is strong evidence that the electrolyte immediately dissociates on being placed in solution and that the ions are the actual carriers of the current. When the ions reach their respective electrodes their charges of electricity are unloaded and they are transformed into the elementary substances; they are then deposited upon the electrode, escape as a gas or react chemically upon the water. Since hydrogen has a valency of one it is said to have one electrical charge and that positive; chlorine ions have one negative charge.

$$\mathrm{HCl, aq.} \rightleftarrows \overset{+}{\mathrm{H}} + \mathrm{Cl'} \qquad \mathrm{NaOH, aq.} \rightleftarrows \overset{+}{\mathrm{Na}} + \mathrm{OH'}$$

$$\begin{array}{ccc} \mathrm{H_2SO_4, aq.} \rightleftarrows \overset{+}{\mathrm{H}} + & \mathrm{HSO'_4} & \qquad \mathrm{NaCl, aq.} \rightleftarrows \overset{+}{\mathrm{Na}} + \mathrm{Cl'} \\ & \downarrow\uparrow & \\ & \mathrm{SO''_4} + \overset{+}{\mathrm{H}}\ . & \end{array}$$

It is evident that in an electrolytic solution the solute is partly in the molecular condition and partly in the ionic state. Water is not a good conductor of electricity, yet it is very slightly dissociated.

$$(99.95\%)\mathrm{H_2O} \rightleftarrows \mathrm{H^+} + \mathrm{OH'}(.041\%)$$

The remark is frequently made, however, that if it is slightly acidified with sulphuric acid it becomes a good conductor. Interpreted in terms of the "electrolytic dissociation" theory, this means merely that the acid is dissociated into hydrogen and the acid radical ions which carry the current.

The student should not confuse the ideas of solubility and electrolytic dissociation. Great solubility does not imply great dissociation.

For purposes of convenience all substances have been divided into three groups—*electrolytes*, *half-electrolytes* and *non-electrolytes*. The term "electrolyte" has been frequently used in two different senses—sometimes referring to the solute and at other times used to designate the conducting solution. It is more properly used in this latter sense. The word "*iongen*" has been proposed as a suitable name for those substances which dissociate when placed in solution. This seems to be more consistent with facts, as salts, acid and bases, with the exception of fused salts, are in themselves non-conductors of the electric current. Solutions of salts and strong acids and bases are included in the class known as electrolytes; solutions of such weak acids and bases, as acetic acid and ammonium hydroxide, which are poor conductors of the electric current, are grouped as half-electrolytes, while all other substances, largely organic, which do not conduct are called non-electrolytes.

Before proceeding with special phases and applications of the theory, it might be well to consider a number of explanations which have been volunteered in an effort to answer the question as to the source of the electric charges possessed by the ions.

Source of Electric Charges.—Le Blanc thinks that in a compound like potassium iodide there remains some chemical energy after the metallic potassium and iodine have chemically combined, and that this chemical energy, through the influence of the solvent, is transformed into electrical energy which is seated in the charges of the ions. By the aid of an electric current during electrolysis it is possible to add to these ions the energy which they originally possessed as neutral substances, when they will separate in the ordinary molecular forms at the electrodes.

According to Nernst, the dielectric constant of a liquid and its dissociating power are in direct proportion. He holds that the forces which bind the ions together to form a molecule are due to electrical attractions between the oppositely charged ions. The specific inductive capacity of water at 20° C. is 81.1 times that of air; therefore, since the ions are supposed to have a constant charge, the force exerted between the ions in a molecule, tending to prevent the dissociation will be 81.1 times less in water than in air. The dielectric constant of ethyl alcohol is 26, for ethyl ether 4.36, and for carbon disulphide 2.6.

The "electron theory," as advanced by J. J. Thomson, suggests that there is only one kind of ultimate particle—the electron, an atom of electricity which has a mass af about one-thousandth that of a hydrogen atom. This theory necessitates a revision of our former notions of the chemical atom. It assumes "that atoms of the various elements are collections (constellations) of these electrons—positive and negative charges held together mainly by their electric attractions, associated with more or less ether." These corpuscles are conceived of as being in a state of rapid vibration. In some atoms the velocities of the electrons (negative charges) may be so great that a corpuscle escapes at once from the atom, thus leaving the atom positively charged; or the reverse may be the case, leaving the atom negatively charged. A negatively charged body contains an *excess* of electrons; a positively charged one, a *defect.* It is thought, for example, that when sodium and chlorine, each representing a particular "constellation" of electrons, combine to form sodium chloride that the two groups of electrons are modified. Now, it is difficult to break up a molecule into atoms out of which it was formed, but comparatively easy to split it in a slightly different manner, so as to leave one electron in *excess* with the chlorine, and a *defect* of one with the sodium, with the result that they become charged positively and negatively, respectively. The organic chemist is familiar with the fact that it may be quite difficult to split a long carbon compound at a particular bond or link, but very easy perhaps to break it at some other link. It follows from the above that "since electrons possess a definite though very small mass, the association with, or removal of, the electric charges from matter causes a difference in its mass.

$$\mathrm{Cl} + \theta \rightarrow \mathrm{Cl}'$$
$$\mathrm{Na} - \theta \rightarrow \underset{+}{\mathrm{Na}}$$

Chlorine has an atomic mass of 35.45; therefore, the mass of a chlorine ion would be 35.451, and the weight of a sodium ion would be .001 less than the atomic weight. Here as elsewhere the student should not confuse fact and theory.

In an article by G. T. Beilby, which recently appeared in The Chemical News, London, some very interesting suggestions are made by the author in regard to the probable source of the energy of solution. The following are extracts from said article: "The solute molecules in a dilute solution of any non-volatile solid, are *solid* molecules sparsly distributed among a multitude of intensely active solvent molecules, the temperature of the solution being frequently many hundred degrees below that at which they could of themselves assume the greater freedom of the liquid or gaseous state. These solute molecules have to a great extent been set free from the constraining effect of their cohesive forces, *but it is important to remember that this freedom has not been attained by the increase of their own kinetic energy as in liquefaction by heat.* Their freedom and the extra kinetic energy they have acquired have in some way been imparted to them by the more active solvent molecules; for, if the solvent could be suddenly removed, leaving the solute molecules still similarly distributed in a vacuous space, they would eventually condense into a solid aggregate. This must be the case, for the non-volatile solute has no measurable vapor pressure at the temperature of the solution. The kinetic energy of the solute molecules is of itself quite insufficient to endow them with the properties of the gaseous or even of the liquid molecule, even when their cohesive forces have been weakened or overcome by separation.

If the energy employed in this separation is not intrinsic to the solute molecule then it must in some way have been imparted by the solvent molecules. It therefore becomes important to compare the energy endowment of one set of molecules with that of the other." * * * "Taking into consideration not only this greater store of energy, but also the much smaller cohesive force of water as compared with the majority of solid solutes, there can be no doubt that the active role in aqueous solutions must be assigned to the solvent, not to the solute molecules.

This leads to the important conclusion that the energy of solution, of diffusion, and of osmosis is due, not to imaginary gaseous energy of the solute, but to the actual liquid energy of the solvent." * * * "The rude mechanical jostling to which the complex molecule is subjected will naturally tend to break it up into simpler portions which are mechanically more stable."

"The view that the phenomena of solution depend on the relative kinetic energy of the solvent and solute molecules appears to apply with special force to the phenomena of dissociation in dilute solutions. Under the gas theory there does not appear to be any reason why the solute molecules should dissociate into their ions. So obvious is this absence of any physical motive that Professor Armstrong has happily referred to the dissociation as "the suicide of the molecules." "With the acceptance of the view that phenomena of solution are largely due to kinetic energy of the solvent molecules, the phenomena of dissociation also appear to take their place as a natural result of this activity, for consider the situation of an isolated molecule (solute), closely surrounded by and at the mercy of some millions of water molecules all in a state of intense activity."

"An ideally perfect solution—that is, a solution of which the physical properties are determined solely by the number of molecules it contains in a given volume—must consist of a solvent and a solute which have no chemical affinity for each other, so that their molecules will neither associate not dissociate in solution. Probably comparatively few solutions will be found which even approximate to this ideal perfection."

It appears as though the two latter theories might be correlated so as to become supplementary.

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APPLICATION OF THEORY.

Electrolysis and Electrical Equivalents.

Experiment I.—Electrolysis.

(*a*) Refer to experiment in which the electrolysis of H_2O was performed through the agency of Na_2SO_4. Interpret the phenomena observed in the light of the "ion theory." Represent the electrolytic reactions by means of equations in which are shown the ions. Explain the formation of free elements at the electrodes.

(*b*) Perform the electrolysis of HCl. Explain mechanism.

Careful measurements have shown that 96,580* coulombs (one "Faraday") of electricity will deposit one *gram-equivalent* of any substance. This quantity of electricity is known as the *electro-chemical* constant. A short rule for determining the *gram-equivalent* is: divide the atomic weight of an element, or the sum of the atomic weights if it is a radical, by its valency; the quotient will represent the number of grams of that substance deposited by 96,580 coulombs. The *electro-chemical equivalent* may be found by dividing the gram-equivalent by 96,580. It is the amount deposited by one coulomb. Example: Atomic weight of oxygen is 16; its valency is 2; therefore 8 grams is the *gram-equivalent*. For silver it is, $107.93 \div 1 = 107.93$ grams. The *electro-chemical equivalent* of silver is, $107.92 \div 96.580 = .0011175$ grams. Recall Faraday's laws.

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* Richards', T. W., value.

Names of Ions.—The following list is based on Walker's system:

Anions.		Cations.	
Cl'	Chloridion	Na'	Natrion (Sodium)
ClO_3'	Chloranion	K'	Kalion
ClO_4'	Perchloranion	NH_4'	Ammonion
NO_3'	Nitranion	Ca''	Calcion
SO_4''	Sulphanion	H'	Hydrion
SO_3''	Sulphosion	Fe'''	Triferrion
S''	Sulphidion	Fe''	Diferrion
$HC_2H_3O_2'$	Acetanion	Cu''	Dicuprion
OH'	Hydroxidion	Ag'	Argention

Some of the most interesting things which are learned in regard to ions by means of experiments in electrolysis are, (*a*) no electrical energy is consumed in the production of ions; their birth is antecendent to the passing of the current, (*b*) they carry electrical charges which are proportional to their relative valencies, (*c*) their relative migration velocities differ greatly, but the migration velocity of a particular ion is independent of the nature of the co-existent ions, and (*d*) the absolute velocity of the most speedy ion is very slow. The following absolute velocities at 18° calculated for infinitely diluted aqueous solutions are given by Kohlrausch. The difference of potential between the electrodes 1 cm. apart was 1 volt.

K = .00066 cm.
NH_4 = .00066 cm.
Na = .00045 cm.
Li = .00036 cm.
Ag = .00057 cm.
H = .00320 cm.
Cl = .00069 cm.
NO_3 = .00064 cm.
ClO_3 = .00057 cm.
OH = .00181 cm.

It is seen that the movement of the ions through practically pure water is very slow. Walker calculates the force required to drive 1 gram of hydrion through water at the rate of 1 cm. per second to be equal to about 320,000 tons weight. It is obvious that the ions experience great resistance to their movements. This is said to be due, at least in part, to the "hydration of the ion," i.e., the comparatively large amount of water which travels with the ions.

CONDUCTIVITIES.

Experiment II. (L. T.) Electrolytes, Half-Electrolytes and Non-Electrolytes.

(Instructions.) By means of a number of conductivity cells (Figs. 26 and 27) and an alternating current suitably applied, determine the relative electrical conductivities of the following substances. On basis of results arrange substances under the three heads suggested above. Sugar ($C_{12}H_{22}O_{11}$) solution, toluene (C_7H_8), NaCl solution, C_2H_5OH, chloroform ($CHCl_3$), HCl solution, NaOH solution, acetic acid ($HC_2H_3O_2$) solution, NH_4OH, distilled H_2O, dilute solution of C_2H_5OH, NH_4Cl solution, HNO_3 solution, $KC_2H_3O_2$ solution, C_6H_6.

Note.—It is suggested that .1N or .5N solutions of acids, bases and salts be used in above experiment.

In view of your experiments, what would you say of the conductivity of organic compounds as compared with inorganic substances in aqueous solution?

There is, accurately speaking, no sharp line of demarcation between these classes. The distinction is based, however, on degree of conductivity. It should be recalled that electrolytes produced abnormal osmotic pressures, abnormal depressions of the freezing point and abnormal lowerings of the vapor pressure; that is, they (solutes) apparently dissociated in water in a manner similar to the dissociation of gases under favorable conditions of pressure and temperature.

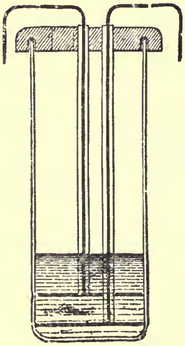


FIG. 26.

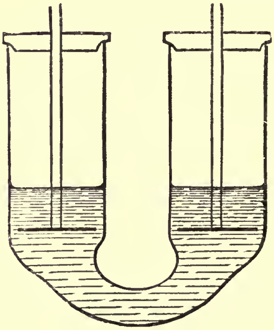


FIG. 27.

$$N_2O_4 \rightleftarrows NO_2 + NO_2$$
$$I_2 \rightleftarrows I + I$$

On the other hand, the non-electrolytes yield normal results relative to osmotic pressure, depression of freezing point, and lowering of vapor pressure. It seems, therefore, that conductivity is due to these little particles into which the molecules are dissociated, namely, anions and cations. And because these ions are attracted to the positive and negative electrodes respectively of an electrolytic cell, they must be oppositely charged. This kind of splitting up of the molecule has been called "electrolytic dissociation" to distinguish it from gaseous dissociation where the particles are not apparently electrically charged.

Other conditions being the same, conductivity depends upon the degree of ionization, i.e., the number of ions present.

Experiment III.—Ionization in Solution.

(*a*) Nature of Solute. Determine relative electrical conductivity of aqueous solutions of the following: NaCl, C_2H_5OH, HNO_3, $CHCl_3$,

KOH, NH_4OH, KNO_3, $NaOH$, Na_2SO_4, $Ca(OH)_2$, HCl, $HC_2H_3O_2$ and $HgCl_2$. Tabulate data under the following heads: acids, bases, salts, organic compounds, so that substances having greatest conductivities will stand at the head of their respective columns.

Is it evident from above that the ionization of different solutes vary greatly? Write the formula for one substance in each column showing the ions formed by its dissociation. What ions are common to all acids? Bases? If the "strength" of acids and bases depends upon the relative concentrations of hydrogen and hydroxidions respectively, which of the above represent the "strong" acids and bases? Indicate by a star placed opposite the formula.

As a general rule, it may be stated that aqueous solutions of salts and the so-called "strong" acids and bases are good conductors because they are largely ionized. Mercuric chloride is an exception, but not the only one. Dissociation of a substance may be said to be one of its specific properties, and, as such, it would be expected that different substances possess this property in varying degrees. The beginner is again cautioned against concluding that because a substance is very soluble that it is very largely dissociated. Sugar is quite soluble, but we have no evidence that it dissociates.

(*b*) (1) Effect and nature of solvent. Proceed as in foregoing experiments to ascertain the relative conductivity of: (1) distilled H_2O, (2) dry $NaCl$, (3) dry $C_{12}H_{22}O_{11}$, (4) dry NaI, (5) aqueous solutions of (2), (3), (4). Using C_2H_5OH, $CHCl_3$, and C_7H_8 instead of water repeat (5).

Add alcohol to a NaCl solution from time to time, and as frequently note effect on the conductivity of the solution. Results?

(*b*) (2) Prepare some perfectly dry HCl gas by bubbling it through concentrated H_2SO_4; run the gas into toluene (C_7H_8) or benzene (C_6H_6) until latter is saturated, then run gas into distilled H_2O; test each of the solutions with litmus paper. Results? Now place the solutions of HCl in two separate and thoroughly cleaned and dried conductivity cells and determine relative conductivity. Results? Does the toluene solution of HCl show any acid properties whatever? Are there any ions in this solution? Your reasons? Set aside this latter solution for future use.

What would you say of the dissociating power of H_2O as compared with other solvents tested?

The nature of the solvent plays a very important role in determining whether a resulting solution will conduct or not, i.e., whether the solute will or will not ionize. Therefore conductivity does not depend alone on either solute or solvent. Water is the most efficient dissociating agent with which we are acquainted.

At ordinary temperatures *pure* substances appear to have small conductivities, providing the transfer is electrolytic. At higher temperatures fused salts and metallic oxides are good electrolytic conductors. It was maintained at one time that only aqueous solutions were good electrolytes, but it has since been learned that certain non-aqueous solutions frequently give higher conductivities. Liquefied NH_3, SO_2 and HCN dissolve salts and make good conductors. Their properties, however, are much more complex than those of water.

A satisfactory and final explanation as to why water or any other solvent acts in such a manner has not been volunteered. It has been suggested as a general rule:

"*When the solvent is associated, the dissolved molecules are mostly simple, and vice versa.*"

There is experimental evidence to support the idea that in pure water there is found in addition to $H_2O \rightleftarrows H^{\cdot} + OH'$, polymerized or *associated* molecules of water with formulæ probably varying from H_4O_2—H_8O_4. Water itself when pure conducts only in a minimum degree. It should be kept in mind that the hydrions and hydroxidions of dissociated water may unite with other oppositely charged ions, and the compound thus formed may or may not dissociate depending upon its nature and the solvent.

It has been calculated that ten to eleven million liters of pure water contain one gram of hydrions and seventeen grams of hydroxidions.

When NaCl is dissolved in water a portion of it dissociates as per the equation, $NaCl \rightleftarrows Na^{\cdot} + Cl'$, but owing to

$$\begin{tikzcd}[row sep=small, column sep=tiny]
\mathrm{H_2O} \rightleftarrows & \overset{+}{\mathrm{OH'}} \arrow[d, shift right] & + & \overset{+}{\mathrm{H}^{\cdot}} \arrow[d, shift right] \\
& \mathrm{NaOH} \arrow[u, shift right] & & \mathrm{HCl}, \arrow[u, shift right]
\end{tikzcd}$$

the dissociation of water the above equations represent the reactions that will undoubtedly occur, as well as the number of different particles present.

(*c*) Effect of dilution. Test the conductivity of glacial acetic acid or concentrated sulphuric acid. Add a few drops of water; test. Repeat operations many times. Record all results. Is ionization increased or diminished by dilution? Write equations showing the dissociation on addition of water to $HC_2H_3O_2$. How many particles are present in the solution? Write similar equations for NaOH and Na_2SO_4.

It is quite obvious that if increased conductivity is due to an increase in ionization in the above experiment that dilution produces a greater degree of dissociation.

Arrhenius established the following law which although not absolutely correct is sufficiently accurate for practical purposes.

"*The degree of dissociation of a substance in a solution is equal to the ratio of the equivalent conductivity of that solution to its equivalent conductivity at infinite dilution.*"

$$y = \frac{\Lambda_v}{\Lambda_\infty}$$

Another law of much importance to the chemist is known as Ostwald's Law of Dilution. It applys to a binary electrolyte, i.e., when each molecule forms two ions. The law involves the mass law.

"*The product of the concentration of the two ions divided by the concentration of the undissociated part is a constant.*"

This law may be represented in formula as follows:

$$(1)\quad Na^{\cdot} + Cl' \rightleftarrows NaCl$$

$$(2)\quad C_3 \,.\, C_2 = K\,C_1$$

$$(3)\quad K = \frac{C_2 \,.\, C_3}{K\,C_1}$$

is known as the "dissociation constant" and its value varies with each solute and solvent and temperature. It states, however, a constant relation which exists between the ions and the undissociated molecules of an electrolyte. The relation of dilution to degree of ionization may be shown by altering the form of the equation. Let y equal the fraction that is dissociated, then $1 - y$ equals the part which is in the molecular condition, and v the volume to which the solution is diluted.

$$(4)\quad C_3 = \frac{y}{v}\,;\; C_2 = \frac{y}{v}\,;\; C_1 = \frac{1 - y}{v}\,.$$

$$(5)\quad \frac{\dfrac{y^2}{v^2}}{\dfrac{1 - y}{v}} = K;\; \frac{y^2}{(1 - y)\,v} = K.$$

It is evident on mere inspection that if we dilute the electrolyte, i.e., increase its volume (v) by addition of the pure solvent, then we diminish all the concentrations of the substances represented in the formula—see (3); but this will affect the numerator more than the denominator because the former is a *product* of two concentrations. If such were true then K would not remain constant, which is contrary to our experimental data. In order then for the value of K to remain constant the concentrations of C_2 and C_3 must become greater through the dissociation of the undissociated molecules represented by C_1. The formula therefore represents that dilution produces a greater degree of ionization.

Although the law of dissociation as given by Ostwald does not apply to strong electrolytes, yet the formula may be taken as practically correct up to a concentration of .01N.

The dissociation constant K is a characteristic of every compound. If the degree of ionization is large for any substance then the value of K will be large and *vice versa*. We shall see later how this "constant" is really a measure of the strength of acids.

The form of the law of dilution suggests a condition of equilibrium as existing between the product of the ions on one side and the molecules on the other. As a matter of fact this is the real statement of the relations existent. The ions are in equilibrium with the undissociated molecules. If the concentration of any of the particles is altered, say C_2 is increased, then some of C_3 will combine with C_2 to increase the value of C_1 until the mathematical form of the equation is re-established. Again, if the value of C_1 should be increased, the reaction would run in such a direction as to increase the values of C_2 and C_3 until original conditions prevail. Such changes are called *reversible*—and the change itself is known as a *balanced action.*

The effect of *temperature* and *pressure* upon ionization is easily anticipated by applying Le Chatelier's Theorem. In some cases the heat of dissociation is positive while in others it is negative.

COLOR OF IONS.

The theory of electrolytic dissociation requires that the color of an electrolyte, i.e., a dilute salt solution shall depend upon the color of its free ions. There is much experimental evidence to support this view.

Experiment IV.—Persistency of the Color of an Ion.

(*a*) Observe the colors of solutions of the following substances as you find them among the "shelf reagents." Write the equations showing the ions formed by dissociation. Tabulate results, stating the color of the respective anions and cations:

$NaCl$, $NaBr$, KNO_3, KCl, Na_2SO_4, $KC_2H_3O_2$, NH_4Cl, KI, $BaCl_2$, $CaCl_2$, KBr, $NH_4C_2H_3O_2$.

(*b*) Now examine solutions of $Cu(C_2H_3O_2)_2$, $CuCl_2$, $Cu(NO_3)_2$, $CuSO_4$; compare the color of the solutions with the substance in the dry solid state; write equations showing ions formed by dissociation; by means of (a) tabulate colors of anions; what ion is the cation common to all the solutions? What is the probable source of the color common to the solutions? Is the color likely due to the salt in the molecular condition? Why? What is the color of anhydrous copper sulphate? (Recall a former experiment.) Note colors of solutions of $Co(NO_3)_2$, $CoCl_2$, K_2CrO_4. State source of color and your reasons for thinking so.

(*c*) Place a small pinch of $CuBr_2$ in a test tube. What is the color of the dry salt? Add a few drops of water. Observe color. Add water to test tube until one-fourth full. Is it probable that the dominant color is due to molecular $CuBr_2$? Your reasons? Now fill the test tube with water. What is the color? Is it similar in color to solutions of copper salts used in (b)? Why was it necessary to dilute the solution to so great a degree to procure final color? Write the formula for Ostwald's Law of Dilution. Interpret above experiment in terms of it.

(*d*) Effect of magnitude of electrical charge on color of ion. Prepare dilute solutions of $FeSO_4$, and $FeCl_3$. Show by means of formulæ the ions formed in the respective solutions. What is the color of the anions in both? Is the iron ion common to both solutions? Is its electrical charge (valence) identical in both cases? Is its energy content identical in both solutions? Would you infer that the latter had something to do with its properties? What are your conclusions in regard to the difference in color of the two solutions? Are the two iron ions identical? In view of (a), (b), (c), would you consider it an extravagant assumption to assume that any particular ion always maintains its identity, i.e., possesses an individual set of chemical and physical properties?

Ostwald in particular has studied this question of the absorption spectra of solutions from the stand-point of the dissociation theory, and the following conclusion was reached:

"That the spectra of dilute solutions of salts containing the same colored ion are identical."

CHEMICAL CONDUCT OF IONS.

With comparatively few exceptions chemical reactions are the result of the mutual interaction of ions.

Experiment V.—Ions Necessary to Chemical Reaction—Acids.

(*a*) Place a portion of the concentrated H_2SO_4 or $HC_2H_3O_2$, which would not conduct the electric current, upon a piece of dry zinc. Results? Dilute the acids with four or five times their volume of distilled water. Results? Explain and write equations showing action of water upon acids and of solutions upon zinc.

(*b*) Pour some of the toluene saturated with dry HCl upon a dry piece of marble. Results? Did the above solution act like an electrolyte? Add a little water to a portion of the toluene solution of HCl; test its conductivity; test its action upon a dry piece of marble. Results? Explain. Equations?

(*c*) Recall or repeat the experiment of mixing dry $NaHCO_3$ and $H_2C_4H_4O_6$ in a mortar. Observe whether any chemical action takes place. Add water to the mixture. Results? Explain in terms of the dissociation theory. Equations?

Concentrated acids are usually very slightly ionized; that is, they yield but few ions, their conductivity is low and their chemical activity as an acid is correspondingly weak. *Acids are substances which when dissolved in water or other dissociating solvents, yield hydrions.* This hydrion is common to all acids and is the source of the acidic properties of the general class of substances known as acids. The *hydrion* is a colorless substance composed of one atom of hydrogen bearing one electrical charge. It has a sour, acid taste and turns blue litmus red. It may transfer its charge to some metals like zinc and magnesium and suffer displacement from the solution. $Zn + 2H^{\cdot} + SO''_4 \rightarrow Zn^{\cdot\cdot} + SO''_4 +$

H_2. It combines with the hydroxidion to form water. Its migration velocity is much greater than that of any of the other common ions, therefore it confers large conductivities upon those solutions in which it is contained, providing there is sufficient concentration of said ions.

It follows that the "strength" of an acid will depend upon the *concentration* of hydrions which it can supply. In other words, those acids whose "dissociation constants" (K) are large, are known as "strong" acids and good conductors, and *vice versa.* Conductivity measurements are approximate measurements of the relative "strength" of acids.

Experiment VI.—"Strength" of Acids.

Determine the conductivities of the following acids in the concentrated and in the diluted conditions: H_3PO_4, H_2SO_4, HCl, $HC_2H_3O_2$, HNO_3. Tabulate results, arranging acids in order of increasing conductivity.

Any process which removes hydrions from a solution or prevents their appearance in same will eliminate all acid properties. Toluene prevented the dissociation of HCl, hence neither conductivity nor acid reaction of the toluene solution of hydrogen chloride.

Experiment VII.—"Strength" Of Bases.

Proceed as in former experiments to ascertain the relative conductivities of 1N. solutions of NH_4OH, NaOH, $Ca(OH)_2$, and KOH. Tabulate results. Write an equation for each substance showing nature of dissociation. Which ion is common to all the solutions?

As in the case of acids, we find solutions of bases giving varying conductivities, depending largely upon their relative degree of ionization. *Bases are substances, the aqueous solutions of which yield hydroxidions.* It is this ion which confers the basic properties upon the class of substances known as bases. The hydroxidion is a colorless substance composed of one atom each of hydrogen and oxygen (hydroxyl), bearing one electrical charge. It possesses a caustic, lye-like taste and turns red litmus blue. It combines with the hydrion to form water. Its migration velocity, though much greater than other ions, is but little more than one-half the velocity of the hydrogen ion. The "strength" of a base will depend upon its "dissociation constant." "Strong" bases will have a constant whose value is comparatively large; "weak" bases, the reverse.

$$
\begin{aligned}
&HCl &&\rightarrow H^{\cdot} + Cl' \\
&HNO_3 &&\rightarrow H^{\cdot} + NO'_3 \\
&HBr &&\rightarrow H^{\cdot} + Br' \\
&NaOH &&\rightarrow OH' + Na^{\cdot} \\
&KOH &&\rightarrow OH' + K^{\cdot} \\
&LiOH &&\rightarrow OH' + Li^{\cdot}
\end{aligned}
$$

Neutralization.—Salts.

$H^{\cdot} + Cl' + Na^{\cdot} + OH' \rightarrow Na^{\cdot} + Cl' + H_2O + 13700$ cals.
$H^{\cdot} + Cl' + K^{\cdot} + OH' \rightarrow K^{\cdot} + Cl' + H_2O + 13700$ cals.
$H^{\cdot} + Cl' + Li^{\cdot} + OH' \rightarrow Li^{\cdot} + Cl' + H_2O + 13700$ cals.

$H^{\cdot} + OH' \rightarrow H_2O + 13700$ cals.

$H^{\cdot} + Cl' + NH^{\cdot}_4 + OH' \rightarrow NH^{\cdot}_4 + Cl' + H_2O + 12200$ cals.
$H^{\cdot} + C_2H_3O'_2 + Na^{\cdot} + OH' \rightarrow Na^{\cdot} + C_2H_3O_2 + H_2O + 13300$ cals.
$H^{\cdot} + F' + Na^{\cdot} + OH' \rightarrow Na^{\cdot} + F' + H_2O + 16200$ cals.

Neutralization is the process whereby the hydrions of an acid and hydroxidions of a base combine to form water.

THERMO-CHEMICAL SUPPORT OF THE DISSOCIATION THEORY.

The "heat of neutralization" of strong acids and bases furnishes one of the strongest supports for the "ion theory." Jones says:

Since all processes of neutralization of completely dissociated acids and bases are the same, the heat of neutralization of all such acids and bases must be a constant, and must be the heat of combination of a gram equivalent of hydroxyl and hydrogen ions.

It may be added, if either the acid or base is "weak," the heat of neutralization will not be 13700 cals, but will vary from that value; it may be more or less.

Change in Volume Support.—Another bit of evidence said to support the theory of solution is the uniform contraction in volume observed during the neutralization of strong acids and bases. When 1000 $cm.^3$ of a normal solution of a strong base are used to neutralize 1000 $cm.^3$ of a strong acid, the resulting mixture has a volume which is always 20 $cm.^3$ less than the sum of the two original volumes. The inference usually made is—the 1 gram of hydrions and 17 grams of hydroxidions occupy a larger volume by 20 $cm.^3$ than 18 grams of water which they form as the result of the neutralization.

A *salt* is formed during the process of neutralization, and if the latter is complete it may be said to be the result of *the union of the cation of the base and the anion of the acid.*

Salts are named, as a rule, according to composition and without regard to their conduct. Recall former classification.

Experiment VIII.—Salts.

(*a*) Formation of an insoluble salt. To a few $cm.^3$ of $AgNO_3$ solution procured from the "shelf reagents," add 5 $cm.^3$ of distilled water. Shake vigorously. Divide into four equal portions, using test tubes as receptacles. To one portion add a few drops of HCl, to another a little $CHCl_3$, to another a few drops of a NaCl solution, to the remaining tube add a small quantity of a $KClO_3$ solution. Record all data. Give equations showing the interaction of ions.

(*b*) Formation of a complex salt. To a few $cm.^3$ of $AgNO_3$ solution add two or three drops of KCN. *Caution.*—KCN is a poison. Add a little more KCN; continue to add until a clear solution is obtained. Add a few drops of HCl. Result? Explain various reactions. Give equations.

(*c*) Repeat above using a solution of $CuSO_4$. Continue to add KCN until solution is colorless. Explain. Equations?

A "*complex salt*" is one which gives a complex ion, for example, $KAg(CN)_2 \rightarrow K^{\cdot} + Ag(CN)'_2$. A "*compound salt*" like $K_2Mg(SO_4)_2$ manifests less tendency to form complex ions. $K_2Mg(SO_4)_2 \rightarrow 2K^{\cdot} + Mg^{\cdot\cdot} + 2SO'_4$. It would be in accordance with facts to state that both "complex" and "compound" salts go through successive steps of ionization.

HYDROLYSIS.

Heretofore we have spoken of water as a neutral substance, but this is far from being true. It will be recalled that water dissociates into hydrions and hydroxidions. If a salt when dissolved in water simply undergoes dissociation the solution is neutral, since there are not present any appreciable amounts of free hydrions and hydroxidions. If, however, the nature of the cation of the salt is such that it forms a weak base when combined with an hydroxyl group, it will combine with the OH ions of the water, and being a weak base, it remains to a great extent in the associated condition. If it should be only slightly soluble, it will be precipitated. This removal of cation of salt and OH ions of water, leaves the anion of the salt and the H ions of the water in the solution, which now possesses an acid reaction due to the free hydrions. If the anion of the salt forms a weak acid when combined with a hydrion, then by a similar line of reasoning this would leave free hydroxidions in solution which would then possess an alkaline reaction.

Experiment IX.—Hydrolysis.

(*a*) Place 5 $cm.^3$ of distilled water in a test tube; test it with litmus paper to assure yourself that it is neutral. Dissolve a small crystal of $AlCl_3$ or $Al_2(SO_4)_3$. Are these "neutral salts"? Test the solution. Results? Explain. Equations?

(*b*) Using distilled water and Na_2CO_3 repeat above experiment. Results? Explain. Equations?

(*c*) Place a small crystal of $SbCl_3$ in the bottom of a test tube; add 5 $cm.^3$ of distilled water; shake vigorously, then add concentrated HCl drop by drop until solution becomes clear after warming. Add from 25 to 50 $cm.^3$ of water. Results? Explain. Give equations.

(*d*) Turn to the experiment in your note book under "Salts," in which you tested with litmus paper solutions of various salts. Some of the results were rather perplexing at the time; can you explain away your previous difficulties?

Hydrolysis may be defined as a case of double decomposition in which water is one of the chemical reagents.

Per Cent Ionized.

(*Calculated at* 18° C.)

Acid.	Per Cent.	Acid.	Per Cent.
HCl, conc.	13.60	HI, .5N, 25° C.	90.00
HCl, 1N	78.40	H_2F_2, 1N	7.00
HNO_3, conc.	9.60	H HS, .1N	.06
HNO_3, 1N	82.10	$H.H_2PO_4$, .5N 25° C.	17.00
H_2SO_4 conc.	0.70	$HC_2H_3O_2$, 1N	.40
H_2SO_4, 1N	51.20	$HC_2H_3O_2$, .1N	1.40
$H.HC_2O_4$, .1N 25° C.	50.30	$HC_4H_4O_6$, 1N 25° C.	8.20
$H.HCO_3$, .1N	0.12	HCN, .1N	0.01
Base.	Per cent.	Base.	Per Cent.
Li OH, 1N	63.00	$Ca(OH)_2$, N/64, 25° C.	90.00
NaOH, 1N	73.80	$Sr(OH)_2$ N/64, 25° C.	93.00
K OH, 1N	78.00	$Ba(OH)_2$, .1N,	75.00
K OH, .1N	86.00	$Ba(OH)_2$, N/64, 25° C.	92.00
NH_4OH 1N	0.40	NH_4OH, .1N	1.40
Salts.	Per Cent.	Salts.	Per Cent.
NaCl, 1N	67.60	$CuSO_4$ 1N	22.00
NaCl, .5N	73.40	NH_4Cl, 1N	74.00
NaCl, .1N	83.90	Zn SO_4, 1N	24.00
$NaHCO_3$, 1N	52.00	Zn Cl_2, 1N	48.00
$NaC_2H_3O_2$, 1N	53.00	Hg Cl_2, 1N	0.90
Na_2SO_4, 1N	44.50	$Hg(CN)_2$, 1N	Small
KCl, 1N	75.00	Ag NO_3, 1N	58.00
KNO_3, 1N	64.00	Ca SO_4, .01N	63.00
$KC_2H_3O_2$, 1N	64.00	$BaCl_2$, .1N	75.00
K_2SO_4, 1N	53.00	$MgSO_4$, .1N	45.00
K_2CO_3, 1N	49.00	$KClO_3$, .5N	79.00

*Water, 0.00001 per cent. ionized.

Experiment X.—Ionic Equilibrium.

Prepare a saturated solution of NaCl. Add concentrated HCl slowly drop by drop, until a white granular precipitate of NaCl appears. Write formulæ showing nature of the dissociation of the NaCl and the HCl. Is there an equilibrium between the ions and the undissociated molecules of a solute? Allow the salt to settle; decant the clear supernatant liquid into another test tube; add C_2H_5OH until a fine granular precipitate of NaCl appears. Explain.

To interpret correctly the above phenomena it is necessary to recall certain principles presented previously. An example may facilitate the interpretation. When NaCl is dissolved in water the ions are in equilibrium with the molecular salt, and further, at a definite temperature there is a constant relation between the two as indicated by the equations which follow:

$$\begin{array}{lcl} NaCl \rightleftarrows Na^{\cdot} + Cl' & \qquad & HCl \rightleftarrows H^{\cdot} + Cl' \\ \ \ C_1 \qquad\ C_2 \qquad\ C_3 & & \ \ C_4 \qquad C_5 \quad\ C_6. \\ KC_1 = C_2.C_3 & & KC_4 = C_5.C_6. \end{array}$$

This is a mathematical expression of the equilibrium. If the solution is saturated then the right and left-hand members of the equation possess their maximum values, for K is constant, i.e., is independent of the concentration of the solution. If the solution is diluted then the value of C_1 becomes smaller. Hence it follows, that in a saturated solution at a given temperature for a given solute the concentration of the undissociated molecules, and the product of the concentrations of the ions are constant. KC_1 is called the "*solubility product*" and is a characteristic of each substance. $C_2 \times C_3$ is sometimes spoken of as the "*concentration product*" or "*ion product.*" If the "solubility product" is exceeded, supersaturation or precipitation will result.

It might be well to mention in this connection that a precipitate is in equilibrium with the undissociated molecules remaining in solution.

$$\begin{array}{rl} Na^{\cdot} + Cl' \rightleftarrows & NaCl\ (Dslvd.) \\ & \quad \uparrow\!\downarrow \\ & NaCl.\ (Ppt) \end{array}$$

Referring again to the above experiment, the value of C_3 was greatly increased by C_6, with the result that C_2, in order to preserve the mathematical form of the equation, became correspondingly small by associating with some of C_3 and C_6 to form NaCl. This in turn increased the value of C_1. When this latter exceeded the "solubility product" of NaCl, salt was precipitated.

SOLUTION TENSION.

Experiment XI.—Displacement of Ions by a "Free Metal."

(*a*) Dissolve 5 grams of $Pb(C_2H_3O_2)_2$ in 100 cm.^{3} of distilled H_2O; place solution in a small Erlenmeyer flask; suspend a piece of zinc in the clear solution; set flask aside to stand for several hours. Note the displacement of lead by the zinc.

$$Pb^{\cdot\cdot} + 2C_2H_3O'_2 + Zn \longrightarrow Pb + Zn^{\cdot\cdot} + 2C_2H_3O'_2.$$

(*b*) Repeat (*a*) using $CuSO_4$ solution instead of $Pb\,(C_2H_3O_2)_2$. Results? Equation?

(*c*) Repeat (*b*) using a piece of clean iron wire bent into the form of a coil. Results? Equation?

(*d*) Dissolve a little $HgNO_3$ in hot water, then dip a coiled piece of copper wire into the solution. Set aside for an hour. Results? Rub wire with piece of filter paper. Results? Equation?

(*e*) Pour 10 cm.^{3} of $AgNO_3$ solution into a crystallizing dish; add a few drops of mercury; set aside for an hour or more. Results? Equation?

In all of the above experiments were the displaced ions, anions or cations?

Experiment XII.—Displacement of Ions by a "Free Non-Metal."

(*a*) To separate solutions of KI and KBr, or NaI and NaBr, add a few drops of "chlorine water." Results? Add a little $CHCl_3$ to each test tube and shake. Results? Explain. Equations?

(*b*) To a solution of KI add a little "bromine water." Results? Add a little $CHCl_3$ and shake. Results? Explain. Equations? In the above experiments were the displaced ions, cations or anions?

The inferences which are drawn as the result of the foregoing experiments are, (a) the metals manifest varying tendencies to press into solution, i.e., the ionic condition, since they are not otherwise soluble; (b) the non-metals relative to one another, behave in a manner very similar to the metals. It is possible to arrange the metals in a series in the order of their "decreasing solution tension."

Alkali metals
Alkaline earth metals
Magnesium
Aluminum
Manganese
Zinc
Chromium
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
(Arsenic)
Copper
Antimony
Bismuth
Mercury
Silver
Palladium
Platinum
Gold

As a general rule, the ions of any metal are displaced from a normal solution by any of the *free* metals which precede it in the above series.

The question undoubtedly arises as to why metals have any such property as "solution tension." The following experiments and discussion may enable the student to understand a little more clearly the nature of this phenomena.

Experiment XIII.—Chemical Energy and Electrical Energy.

(*a*) Prepare a cold dilute aqueous solution of H_2SO_4 (4 of H_2O to 1 of acid). Pour the solution into a small beaker. Suspend a strip of clean zinc in the solution; by means of a copper wire connect the zinc with one of the binding posts of a galvanometer or a volt-meter. Read volt-meter. Is there evidence of much chemical action between zinc and H_2SO_4? Bind another copper wire to which is attached a copper strip to the other binding post; suspend copper strip in the solution in such a manner as not to touch zinc strip. Read volt-meter. Results? Is there more or less evidence of chemical action in the beaker than when previously examined? Observe and record phenomena manifested by this typical cell. Did either the solution or the metals contain electricity originally? What is the probable source of the electrical energy? Place a small quantity of "granulated" zinc in the beaker containing the acid solution after removing the strips of Cu. and Zn.; test the escaping gas by means of a lighted match. Results? When chemical action has ceased, remove excess of zinc and once more insert the strips of Zn. and Cu.; take the reading of the volt-meter. Explain. The beaker now contains a solution of what? Evaporate a portion of the solution to dryness. Is it $CuSO_4$? Your reasons?

(*b*) The above experiment may be repeated by substituting for zinc the following metals, iron, copper, lead, aluminum and others as desired. Arrange the metals in order of their increasing *electro-motive force.* (E.M.F.).

The student is familiar with the fact that when heat energy is contributed to solids or liquids in sufficient quantities, the molecules pass into the space above the liquid, and if it be a closed system, equilibrium is established for a given temperature, when the pressure of the vapor is equal to the vapor-tension of the substance. Increase the amount of internal energy of the substance, i.e., raise its temperature, and it is obvious that its vapor-tension is also increased.

Every metal has a certain solution-tension which tends to push its particles into solution in the form of ions. The metal will continue to dissolve until its solution-tension is in equilibrium with the solution-pressure of the ions. Since energy can not come from nothing, it is said that the chemical energy or the free energy of the system is transformed into the electrical charges of the ions. Metals yield cations, and non-metals—anions.

Now it is maintained by Nernst and others that the solution-tension of substances is analogous to vapor-tension. An application of the theory of "electrolytic solution-tension" will reveal the points of analogy as well as the differences.

If we dip a piece of metal, say zinc, into pure water, then owing to the solution-tension of the metal some ions will pass into solution. These ions are charged with positive electricity. Since both kinds of electricity must be simultaneously produced whenever electrical energy comes into existence, the metallic zinc becomes negatively electrified. The solution is now positively electrified and the metal negatively electrified. The positively-charged ions are attracted by the negatively-charged metal, so that a *difference of potential* is established. The metal will, however, continue to press into solution, thereby acquiring a lower potential, until, as mentioned above, the solution-tension is in equilibrium with the solution pressure of the ions. The solution and the metal now have their greatest difference of potential. The "*single potential*" of metals immersed in pure water obviously depends upon their respective solution-tensions. Suppose we now dip a metal like silver into a solution of its ions which have a greater ionic solution-pressure than the metal's solution-tension, this will result in the deposition upon the metal of some of its ions. The metal will become positively electrified and the solution negatively electrified.

Again, if we place a metal in a solution whose ionic solution-pressure is just equal to its solution-tension, equilibrium is established at once. Ions will neither be formed nor deposited, hence there will be no difference of potential between metal and solution.

In the above discussion we have referred alone to the solution-tension of *metals* which form positive ions. Le Blanc says, that as far as we know, all substances capable of yielding negative ions have a high solution-tension. This would leave a free non-metal like chlorine positively charged.

We immediately infer that as the result of solution-tension, metals and non-metals acquire a definite electro-motive force, when placed in pure water or a solution (usually a normal solution) containing their respective ions. This E.M.F. is frequently called the "single potential" of metals or non-metals.

"*The tendency toward chemical reaction and its accompanying transformation of energy in a cell is measured by the E. M. F. or voltage.*" —Lehfeldt's Electro-Chemistry.

We have considered the questions of solution-tension, the production of "single potentials" and the E.M.F. of a cell, but we have not considered in detail the probable source of energy of which the foregoing are manifested forms. This energy is evidently, at least in part, derived from the chemical energy of the system. It was thought for some time that the whole of the chemical energy was converted into electrical energy, but this assumption is by no means justified by the facts. This is only true in the case of cells whose E.M.F. do not vary with temperature. In certain types of cells a portion of the chemical energy is evolved as heat, the cell becoming warmer as the cell continues in action; in other types the electrical work done exceeds the chemical energy spent, i.e., heat is absorbed and transformed into electrical energy.

"Measurement of electro-motive force may then be looked upon as a means of determining the change of the free energy in a chemical reaction."—Lehfeldt's Electro-Chemistry.

The E.M.F. is a measure of the chemical energy of a system when the process is reversible, i.e., when the system is neither warmed nor cooled by the reaction which produced the E.M.F.

TABLE OF SINGLE POTENTIALS.

(The free metal is placed in a normal solution of its ions.)

K = (+ 2.9)
Na = (+ 2.54)
Ba = (+ 2.4)
Sr = (+ 2.3)
Ca = + 2.28
Mg = + 1.21
Al = + 1.00
Mn = + .80
Zn = + .493
Cd = + .143
Fe = + .063
Tl = + .045
Co = — .045
Ni = — .049
Sn = — .07 ?
Pb = — .129

H = — .277
Cu = — .606
As = — .62 ?
Bi = — .67 ?
Sb = — .74 ?
Hg = — 1.027
Ag = — 1.048
Pd = — 1.07 ?
Pt = — 1.14 ?
Au = — 1.35 ?
I = + .797
Br = + 1.270
O = + 1.396?
OH = + 1.396?
Cl = + 1.694
NO_3 = +1.75

SO_4 = +1.90

It will be observed that the relative positions of the *free metals* in the "solution-tension" series and the "E.M.F." series are identical. The order in which the metals occur in this series is especially significant, inasmuch as it represents the relative *chemical activities* of the *free metals*. All of the metals in the fore part of the list readily oxidize when exposed to the air; while those in the latter part of the list do not. It follows from this that the former metals will be reduced with difficulty from their oxides, while the reverse will be true of the latter. The arrangement expresses the combining relations of the metals with regard to other elements as well as oxygen. None of the metals in the fore part of the list are found free in nature. It should be remembered in this connection that all of these same metals can displace hydrogen from an acid, while those which succeed hydrogen in the list and are unable to displace hydrogen are found free in nature. Other relationships will be found represented by this series.

HEAT OF IONIZATION.

Lithium = + 261000 joules.
Potassium = + 257000 joules.
Sodium = + 237000 joules.
Strontium = + 244000 joules.
Calcium = + 226000 joules.
Magnesium = + 225000 joules
Aluminum = + 165000 joules.
Manganese = + 102000 joules.
Zinc = + 69500 joules.
Cadium = + 34600 joules.
Iron (ferrous) = + 42400 joules.
Thallium = + 3400 joules.
Cobalt = + 31700 joules.

Nickel = + 29400 joules.
Tin = + 2900 joules.
Lead = + 2900 joules.
Hydrogen = — 2300 joules.
Copper = — 37200 joules.
Mercury (Hg') = — 86900 joules.
Silver = — 110900 joules.

Chlorine = + 167400 joules.
Bromine = + 121000 joules.
Iodine = + 57500 joules.
Oxygen (1/4 O_2) = + 88600 joules.

Ostwald (Lehrbuch. d. allg. Chem.) has calculated the "heat of ionization" of *one equivalent* for a number of metals. The above table is quoted from his work.

"The heat of ionization of hydrogen is so small as almost to lie within the margin of errors, and may be ignored. Hence, the approximate rule, that the heat of ionization of a metal is practically equal to its heat of solution in dilute (i.e., completely dissociated) acid."—Lehfeldt's Electro-Chemistry.

After inspecting above table it is evident that some of the ions possess more available energy than when in the condition of the *free* metal; other ions, the reverse.

CHAPTER XV.

THE NON-METALS, OR ACID-FORMING ELEMENTS.

THE HALOGEN GROUP.

(THE CHLORINE FAMILY.)

Fluorine,	F,	19
Chlorine,	Cl,	35.45
Bromine,	Br,	79.96
Iodine,	I,	126.97

These four elements compose what is known as a "natural group"; the members are closely connected by a similarity of chemical properties; i.e., they resemble one another in their chemical relations, and by combination with identical substances, produce a series of corresponding compounds which resemble each other in their respective chemical properties.

The members of this group are usually termed the *halogens*, because of their tendency to produce salts resembling sea-salt in their composition. These salts are called *haloid salts* or simply, *halides.*

FLUORINE, F.

At. Wt. 19 Mol. Wt. 38.

Preparation and Properties.—This element is not found free in nature. The chief sources are calcium fluoride, CaF_2, commonly known as *fluorspar* and *cryolite*, AlF_3 $3NaF$. The latter mineral is found in relative abundance in Greenland.

Fluorine is a pale yellowish-green gas with an unpleasant odor like chlorine. Although fluorine does not combine with oxygen it shows a great affinity for hydrogen, with which it unites explosively, even in the dark. In fact, so great is the affinity of fluorine for hydrogen that many compounds which contain the latter are decomposed when brought into contact with it. It is recorded that Moissan, who prepared it in 1886, dropped some of the liquid fluorine on the wooden floor of the laboratory when the wood immediately burst into flame. Because of its remarkable chemical activity, it is exceedingly difficult to prepare. Moissan prepared it by electrolysis of pure liquid H_2F_2 (—25° C. to—50° C.), mixed with a little KF.

$$H + F \longrightarrow \overline{HF} + 37{,}600 \text{ cal.}$$

Hydrogen Derivatives.

Experiment I.—Preparation and Properties of Hydrogen Fluorine.

To a gram of powdered CaF_2 in a test tube add 3 cm.^{3} of concentrated H_2SO_4; heat the tube gently; test the effect of the evolved gas upon a piece of moistened blue litmus paper. Dip a glass rod into a few cm.^{3} of NH_4OH in a test tube; hold rod in evolved gas. Results? After the test tube has been thoroughly cleaned, observe the effect of the gas upon the inside surface of the glass. Write equations indicating nature of above reactions.

Caution.—**The above experiment should be performed in the hood. The gas must not come in contact with the skin nor be breathed.**

Experiment II.—Etching of Glass with Hydrofluoric Acid.

Spread a smooth thin layer of paraffin wax upon one side of a piece of glass, about 10 cm. square; allow the wax to cool and harden; by means of the sharp end of a file or any pointed instrument, cut through the wax to the glass, making any chosen design. Cover the bottom of a shallow lead dish with CaF_2; add sufficient warm H_2SO_4 to moisten powder in dish; place glass plate, waxed side downward, upon the lead dish; warm dish gently but do not melt paraffin. After 10 min. remove heat, and cool dish; remove glass plate and wash off the wax. Has the gas, H_2F_2, evolved affected the glass plate? Equation?

Caution.—Use the greatest care to avoid breathing the gas and to prevent the acid from coming in contact with skin. Perform experiment in the hood.

Experiment III.—Formation of Silicon Tetrafluoride by the Action of H_2F_2 on Silica.

Mix 1 gram of silica, SiO_2 (sand), with 1 gram of CaF_2; place the mixture in a test tube; add a little concentrated H_2SO_4; heat gently. Expose a drop or film of H_2O to the action of the fumes of $Si\,F_4$; observe the milky appearance of the water due to the formation of silicic acid, H_4SiO_4.

$$\begin{aligned}
&(1)\ CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + \overline{H_2F_2},\\
&(2)\ SiO_2 + 2H_2F_2 \longrightarrow \overline{SiF_4} + 2H_2O,\\
&(3)\ 3SiF_4 + 4H_2O \longrightarrow 2H_2Si\,F_6 + H_4Si\,O_4.
\end{aligned}$$

The fluorides of lithium, sodium, potassium, ammonium, silver, mercury, iron, aluminum and tin are soluble in water.

CHLORINE Cl.

At. Wt. 35.45 Mol. Wt. 70.9.

Preparation and Properties of Chlorine.

Experiment I.—Review the previous experiments with chlorine. Fix in mind the physical and chemical properties of the elementary substance.

Hydrogen Derivatives.

Experiment II.—Preparation and Properties of Hydrogen Chloride.

Recall the facts about hydrogen chloride. Compare its properties with the corresponding hydrogen compounds of the other halogens. These hydrogen compounds are styled the *hydrogen halides.*

$$H + Cl \rightarrow HCl + 22{,}000 \text{ cal.}$$

All chlorides, with the exception of silver, mercury (ous), lead and a few basic chlorides like $BiOCl$ and $SbOCl$ are soluble in water. $PbCl_2$ is slightly soluble in cold water and easily soluble in hot water.

Oxygen Derivatives of Chlorine.

Experiment III.—Preparation of Sodium Hypochlorite and Hypochlorous Acid. Oxidizing Power of Hypochlorous Acid—Bleaching.

(*a*) Dissolve 3 grams of $NaOH$ in 20 cm³. of H_2O; pass chlorine into the *cold* dilute solution, but do not saturate it. The probable reaction may be indicated by the following equation:

$$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O.$$

(*b*) Divide the solution into two parts; to one part add dilute H_2SO_4; observe the odor; suspend a piece of cheap red calico and a strip of litmus paper in the acidulated solution for a day; then observe the bleaching effect of hypochlorous acid, $HClO$ upon paper and calico. Write equations.

Ascertain the bleaching properties of a non-acidulated solution of $NaOCl$ by repeating above, using the second portion of the solution. After removing paper and calico, add a few drops of the solution to an indigo, $C_{16}H_{10}N_2O_2$, solution. Effects? Add a few cm.³ of dilute H_2SO_4 to solution, then add 3 cm.³ of the solution to the indigo; observe the bleaching effect. Equations explaining activity of HCl are as follows:

$$2HClO \rightarrow 2HCl + 2O + 18{,}600 \text{ cal.}$$
$$C_{16}H_{10}N_2O_2 + 2O \rightarrow 2C_8H_5NO_2 + 1{,}800 \text{ cal.}$$

$$C_{16}H_{10}N_2O_2 + 2HClO \rightarrow 2C_8H_5NO_2 + 2HCl + 20{,}400 \text{ cal.}$$

Experiment IV.—Bleaching Powder ("Chloride of Lime").

Place 5 grams of chloride of line ($Ca(OCl)_2 + CaCl_2$) in a flask; add 20 cm.³ of H_2O and shake thoroughly; filter. Using the clear filtrate, repeat Exp. III. Do not neglect to acidulate solution or moisten objects to be bleached with very dilute H_2SO_4(1 drop in 25 cm.³ of H_2O).

Experiment V.—Preparation and Properties of Potassium Chlorate.

(*a*) Dissolve 3 grams of KOH in 10 cm.³ of H_2O; saturate the boiling solution with chlorine; cool the solution and observe the formation of crystals of potassium chlorate, $KClO_3$. Devise a method for proving that this substance is identical with the $KClO_3$ (solid) found upon the end shelves. Equations?

(*b*) $KClO_3$ as an oxidizer. Mix a small quantity of powdered $KClO_3$ with a little powdered charcoal; place the mixture upon the cover of a crucible and heat gently. Results? When the cover has cooled, place it in a small beaker which contains 25 cm.³ of H_2O; allow the products of the fusion to dissolve; filter; add a few drops of the filtrate to 2 cm.³ of $AgNO_3$; if a white precipitate forms which turns dark on exposure to light it is AgCl. Explain by use of equations.

Experiment VI.—Chloric Acid. Chlorine Dioxide.

(*a*) Place a small crystal of $KClO_3$ in the bottom of a test tube; add a few drops of strong H_2SO_4; point the mouth of the tube away from your face, then heat cautiously; the explosive action is due to the presence of a yellow gas, chlorine dioxide, ClO_2, which is violently explosive owing to its ready decomposition into chlorine and oxygen, with liberation of much heat.

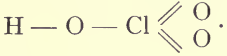
$$\begin{aligned} 2KClO_3 + H_2SO_4 &\rightarrow 2HClO_3 + K_2SO_4, \\ 4HClO_3 &\rightarrow 2H_2O + 4ClO_2 + 2O, \\ 2HClO_3 + 2O &\rightarrow 2\ HClO_4; \end{aligned}$$

or

$$\begin{aligned} 3HClO_3 &\rightarrow HClO_4 + \overline{2ClO_2} + H_2O, \\ 2ClO_2 &\rightarrow \overline{Cl_2} + \overline{2O_2}; \end{aligned}$$

again,

$$6KClO_3 + 3H_2SO_4 \rightarrow 2HClO_4 + 4\overline{ClO_2} + 3K_2SO_4 + 2H_2O.$$

Chloric acid—Structural formula: 

(*b*) Oxidizing action of chloric acid (ClO_2).

Powder 1 gram of $KClO_3$; place the powder upon a sheet of paper and mix with it 1 gram. of sugar; put the mixture upon an iron plate; allow a drop of strong H_2SO_4 to drop from the end of a glass rod upon the mixture. Result?

Note.—White gunpowder is a mixture of $KClO_3$, $K_4Fe(CN)_6$ and $C_{12}H_{22}O_{11}$.

$$HClO_3, Aq \rightarrow HCl, Aq + \overline{3O} + 15{,}300 \text{ cal.}$$

(*c*) Explosive conduct of chlorates. Place very small quantities of $KClO_3$ and sulphur in a mortar; rub the mixture vigorously with the pestle. Sharp explosions result from the friction. As a rule, should chlorates be pulverized with other substances?

All chlorates are soluble in water.

Experiment VII.—Perchlorates and Perchloric Acid.

Perchlorates may be formed by suitably heating chlorates; corresponding chlorides will be formed simultaneously. When either $NaClO_3$ or $KClO_3$ is heated oxygen is evolved; if the operation is stopped when one-third of the oxygen has been liberated, the chloride and the chlorate of the metal remain in the fused mass. The more soluble chloride may be dissolved out from the mass.

$$2\ KClO_3 \rightarrow KClO_4 + KCl + \overline{O_2}$$
$$KClO_4 \rightarrow KCl + 2\overline{O_2}.$$

Perchloric acid, $HClO_4$, may be formed by the action of strong H_2SO_4 on perchlorates. Equation?

$$HClO_4,\ Aq \rightarrow HCl,\ Aq + \overline{2O_2} + 700\ \text{cal.}$$

Structural formula for $HClO_4$?

BROMINE, Br.

At. Wt. 79.96 Mol. Wt. 159.92.

Preparation and Properties of Bromine.

Experiment I.—(Hood.)

Mix 2 grams of powdered MnO_2 with an equal weight of pulverized NaBr or KBr. Introduce the mixture into the test tube used when preparing oxygen from $KClO_3$ and MnO_2; add a few cm.³ of strong H_2SO_4; heat gently and conduct the gas into a 50 cm.³ flask which is nearly immersed in cold water. Observe color, odor and relative density of the gas. When one or two drops of the bromine gas have condensed in flask, conduct the bromine into a test tube containing 15 cm.³ or 20 cm.³ of H_2O. Compare the drop of condensed bromine vapor with the liquid bromine found on side shelf. If the H_2O in the test tube was not saturated with bromine, add a drop of the liquid bromine to the bromine water (H_2O + Br.); shake thoroughly. What is the color of the solution (bromine water)? Test the action of the solution on litmus paper. To one portion of the solution add 2 cm.³ of ether; to a second portion 2 cm.³ of carbon disulphide; and to a third portion, 2 cm.³ of chloroform; shake each tube vigorously. Results?

The following partial equations may assist in interpreting the reactions involved in preparing bromine:

$$NaBr + H_2SO_4 \rightarrow Na_2HSO_4 + (H\ Br).$$
$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + (O).$$
$$2HBr + O \rightleftarrows H_2O + \overline{Br_2}.$$

or

$$4HBr + MnO_2 \rightarrow MnBr_2 + 2H_2O + \overline{Br_2}.$$
$$MnBr_2 + H_2SO_4 \rightarrow MnSO_4 + \overline{2HBr}.$$

Note.—If larger quantities of bromine are to be prepared a retort and a receiving flask may be substituted for the above apparatus.

Experiment II.—Substituting Power of Chlorine as Compared with Bromine.

(*a*) Dissolve a very small crystal of NaBr or KBr in 15 cm.³ of water in a test tube; add a few cm.³ of chlorine water (side shelf); divide the solution into two parts. Heat one portion gently and note the change in color. Explain.

(*b*) To the second portion add 2 cm.³ of CS_2; shake thoroughly. Results? Equations? Which of the two—chlorine or bromine—has the greater affinity for sodium?

Exp. III.—Displacement of Sulphur from Hydrogen Sulphide.

Prepare a saturated solution of bromine by adding a drop of liquid bromine to 10 cm. of H_2O; pass H_2S through the solution until the brown color due to the presence of bromine has disappeared. Is there any evidence of the presence of free sulphur? Filter the solution; boil the filtrate until the fumes will not darken a piece of filter paper moistened with a solution of lead nitrate; test the filtrate with the litmus paper. To 2 cm.³ of $AgNO_3$ add H_2S; repeat, using a few drops of the above filtrate. Equations for all reactions? What substance is produced by the displacement of sulphur from H_2S by bromine? Recall the similar conduct of chlorine in an analogous experiment.

Hydrogen Derivatives.

Experiment IV.—(Hood.) Preparation and Properties of Hydrogen Bromide—Preliminary.

Pulverize about 3 grams of NaBr or KBr, and place it in a test tube; add sufficient strong H_2SO_4 to thoroughly moisten powder; heat *gently;* blow your breath across the mouth of the tube. Results? Dip a glass rod into NH_4OH, then hold rod near mouth of test tube. Results? Hold a moistened piece of blue litmus paper in the evolved gas. Results? What is the color of hydrobromic acid, HBr?

What hydracids studied previously conduct themselves in a similar manner toward the identical tests? Write the equations for the above reactions.

$$NaBr + H_2SO_4 \rightarrow NaHSO_4 + \overline{HBr}.$$

What is the effect of increasing the temperature of the mixture in the test tube? What is the colored gas which makes its appearance?

$$NaBr + H_2SO_4 \rightarrow \underline{NaHSO_4} + (HBr),$$
$$2HBr + H_2SO_4 \rightarrow \overline{SO_2} + \overline{Br_2} + H_2O.$$

H_2SO_4 acts as an oxidizing agent. Was either free fluorine or chlorine observed during the preparation of their respective hydracids from corresponding salts by the use of H_2SO_4?

Experiment V.—Laboratory Source of Hydrogen Bromide. Hydrobromic Acid.

Into a test tube which has been provided with a stopper and a delivery tube, introduce 5 grams of powdered NaBr or KBr; add sufficient concentrated phosphoric acid, H_3PO_4, to cover the powder; shake until the two substances are mixed thoroughly; fit stopper and delivery tube into place; heat tube gently; collect the evolved gas in 5 cm.^{3} of H_2O in a test tube the mouth of the delivery tube should be about .2 cm. above the surface of the water.

Is there any evidence of the presence of free bromine? In what particular respect is H_2SO_4 different from H_3PO_4 in its action on bromides? The acid solution may be tested as in Experiment IV. Add a few drops of the solution to a little sodium carbonate. Results? Repeat the foregoing experiment, using a few cm.^{3} of $AgNO_3$. Results?

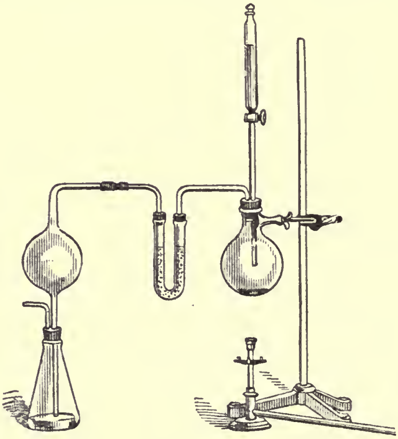


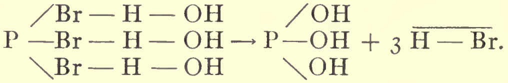
FIG. 28.

If the acid solution is saturated, its effect on a piece of zinc should be ascertained. Wrap a piece of platinum wire around the zinc. Why? Equations?

$$H + Br \rightarrow \overline{HBr} + 8400 \text{ cal.}$$

Experiment VI.—Optional. Preparation of Pure Hydrobromic Acid.

Note.—When phosphorous and bromine are mixed, they combine energetically forming phosphorous tribromide (PBr_3). Pure HBr is prepared by hydrolysis of this substance.



$$P\begin{array}{l} \diagup Br - H - OH \\ -Br - H - OH \\ \diagdown Br - H - OH \end{array} \rightarrow P\begin{array}{l} \diagup OH \\ -OH \\ \diagdown OH \end{array} + 3\,\overline{H - Br}.$$

The preparation of the acid may be conducted as follows: The ordinary funnel of a 300 cm.^{3} generating flask is displaced by a dropping funnel; the flask is connected in series with two U-tubes (or see Fig. 28); the U-tube next to the flask should be half filled with glass beads which have been moistened and rolled in red phosphorous; the second tube should be about one-fourth filled with water to absorb the HBr. The mouth of the tube delivering the gas to the tube should be above the surface of the water. Charge the generating flask with 5 grams of red phosphorus and enough water to barely cover the latter. (It is suggested that 5 grams to 10 grams of clean sand be added with the charge.) Pour 10 $cm.^3$ of bromine (liquid) into the funnel; when apparatus has been assembled properly, allow the bromine to fall on the phosphorus drop by drop. The union of the bromine and phosphorus will be accompanied by a flash of light. (Can you suggest a reason for using red instead of yellow phosphorus?) After the water in the flask has been saturated with the HBr, the latter will escape into the U-tube and eventually be absorbed in the water contained in the most remote U-tube. If too little water is present in the flask, crystals of PBr_3 will clog the apparatus; the addition of a few drops of water will prevent their formation. The acid properties of the solution of the gas may be tested as previously. If convenient its conductivity may be determined.

The bromides are easily soluble in water with the exception of silver, mercury (ous) and lead. $PbBr_2$ is slightly soluble in cold water and easily soluble in hot water.

Oxygen Derivatives of Bromine.

Note.—No oxides of bromine have been prepared.

Experiment VII.—Preparation of Sodium Hypobromite and Hypobromous Acid.

(*a*) Dissolve 3 grams of NaOH in 20 $cm.^3$ of H_2O; add a few drops of liquid bromine to the cold dilute solution. Observe the disappearance of the color of the bromine. The bromine should be added drop by drop, but not in a sufficient quantity to saturate the solution.

$$2NaOH + Br_2 \rightarrow NaBr + NaBrO + H_2O.$$

(*b*) Divide the above solution into two parts. To one portion add dilute H_2SO_4; observe the color and odor of the evolved gas. The following partial equations probably represent the stages of the reaction:

$$NaBr + NaBrO + H_2SO_4 \rightarrow Na_2SO_4 + (HBr) + (HBrO).$$
$$HBr + HBrO \rightarrow H_2O + \overline{Br_2}.$$
Adding, $NaBr + NaBrO + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + \overline{Br_2}.$

(*c*) Repeat (*b*) using acetic acid instead of H_2SO_4. Use slight excess of acid. Note that bromine is liberated. Write the structural formulæ for NaBrO and $NaBrO_3$.

Experiment VIII.—Preparation and Properties of Potassium Bromate.

Dissolve 3 grams of KOH in 10 $cm.^3$ of H_2O; saturate the solution with bromine; heat to boiling. When crystals make their appearance, dissolve them in H_2O; add a few drops of liquid bromine; boil to crystallization; dissolve crystals in the smallest quantity of water; pour the solution into a crystallizing dish. The $KBrO_3$ crystals may be separated from the more soluble KBr crystals by crystallization. Equation?

Experiment IX.—Bromic Acid. Interaction of Bromic and Hydrobromic Acids.

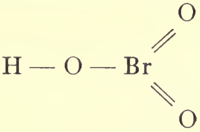
(*a*) To a solution of $NaBrO_3$ or $KBrO_3$, add dilute H_2SO_4. Is bromine liberated? Equation?

(*b*) To a solution containing $KBrO_3$ add dilute H_2SO_4. Is bromine liberated? Equations?

The following thermo-chemical equation gives an approximate idea of the oxidizing power of bromic acid:

$$HBrO_3, Aq \rightarrow HBr, Aq + \overline{3O} + 15{,}000 \text{ cal.}$$

Structural formula for hydrobromic acid:



IODINE. I.

At. Wt. 126.97 Mol. Wt. 254.8 (185°–600°).

Preparation and Properties of Iodine.

Experiment I.—

(*a*) Mix 2 grams of powdered MnO_2 with an equal weight of pulverized NaI or KI; place the mixture in an evaporating dish; add sufficient concentrated H_2SO_4 to moisten the mixture thoroughly; clamp an inverted funnel over the evaporating dish in such a position that all vapors from the dish will escape through the stem of the funnel. Heat the dish gently. A dense vapor will be set free. Observe color, odor and relative density of the vapor before it condenses upon the sides of the funnel. Continue to heat dish until colored vapor ceases to be evolved. After cooling funnel, scrape crystals into a clean beaker to be used for following experiments.

(*b*) Resublimed iodine. Place a few of the crystals in a flask; heat the bottom of the flask gently to volatilize the iodine which crystallizes upon the cooler portions of the flask. Does the iodine fuse before becoming a vapor? What are such processes called?

(*c*) Test the solubility of iodine in each of the following solvents: H_2O, C_2H_5OH, $CHCl_3$, $(C_2H_5)_2O$, CS_2, and a KI solution. Recall a similar experiment under subject of "Solutions."

(*d*) Triturate .3 gram of starch and 20 cm.³ of H_2O in a mortar until they are thoroughly mixed. Pour this mixture into 100 cm.³ of boiling water; boil the mixture for about five minutes. Add a few drops of the cold starch emulsion to a few cm.³ of a KI solution of iodine; heat the mixture. Does the color disappear? Cool. Results? The compound formed with the characteristic blue color is known as *starch iodide.* Iodine is used to detect the presence of starch, and *vice versa.*

Note.—Bottle the starch emulsion and preserve it for future use.

The solution of iodine in alcohol is known as the *tincture* of iodine. The brown color of the tincture is attributed to the fact that the iodine and alcohol are in a loose state of combination; likewise iodine dissolved in a KI solution is supposed to form a definite compound:

$$2KI + I_2 \longrightarrow 2KI_3.$$

On the other hand, the blue substance, starch iodide, referred to as a compound, is not a chemical compound but merely a solution of iodine in starch.

Experiment II.—Substituting Power of Chlorine and Bromine as Compared with Iodine.

(*a*) Dissolve a very small crystal of NaI or KI in 15 cm.^{3} of water in a test tube; divide it into two portions; to one portion add a few drops of chlorine water; heat gently and observe the change in color; add a few drops of the solution to a little of the starch solution. Results? Shake up the rest of the solution with 3 cm.^{3} of CS_2. Results? Equations?

Note.—An excess of chlorine water decolorizes a solution of iodine in CS_2.

(*b*) Repeat (*a*) using the second portion of the solution and bromine water instead of chlorine water. Results? Equations?

In view of the above and previous experiments what do you infer in regard to the relative affinities of the halogens for hydrogen? Arrange them in the order of their increasing affinity.

Experiment III.—Potassium Dichromate Liberates Iodine from an Acidified Solution of an Iodide.

To a dilute solution of KI add CS_2; shake. Results? Acidify the solution with a little dilute H_2SO_4, and add a few drops of a $K_2Cr_2O_7$* solution; agitate the mixture. Results?

Note.—Bromine is not liberated from bromides by above process. Test. Equations?

Experiment IV.—Iodine is Liberated by the Oxidizing Action of Sulphuric Acid.

Place a small crystal of NaI or KI in a test tube; add 3 cm.^{3} of concentrated H_2SO_4; heat gently. Observe the color and odor of the evolved gas. Identify it. Ascertain whether hydriodic acid, HI, is evolved or not.

$$\begin{aligned}KI + H_2SO_4 &\rightleftarrows KHSO_4 + (HI),\\ 2HI + H_2SO_4 &\rightleftarrows SO_2 + I_2 + H_2O,\\ 6HI + H_2SO_4 &\rightleftarrows S + 3I_2 + 4H_2O,\\ 8HI + H_2SO_4 &\rightleftarrows H_2S + 4I_2 + 4H_2O.\end{aligned}$$

---

* Sodium nitrite may be sustituted for $K_2Cr_2O_7$.

Compare the above reaction with the action of H_2SO_4 on CaF_2, NaCl, NaBr. Arrange the hyrdascids of the halogens in the order of their increasing stability toward oxidizing agents.

Experiment V.—Displacement of Sulphur from Hydrogen Sulphide.

To 2 grams of powdered iodine in a flask fitted with a cork containing a single perforation add 20 cm.^{3} of H_2O; pass H_2S through the mixture until iodine disappears. Proceed with experiment as per directions Exp. III, "Bromine."

Hydrogen Derivatives.

Experiment VI.—Preparation and Properties of Hydrogen Iodide. Hydriodic Acid.

(*a*) Follow directions given in Exp. V., "Bromine," substituting the words iodide and iodine for bromide and bromine, respectively. Equations?

(*b*) Pure HI may be prepared by a process similar to that used in the preparation of pure HBr—Exp. VI., "Bromine." Use the same apparatus. The flask may be charged with a mixture of iodine and water (4 to 1), and the red phosphorus (stirred to a paste with water) allowed to fall slowly on the iodine, drop by drop.

Another method, using same apparatus, is as follows: Mix the red phosphorus and iodine (10 to 1 by weight) in a dry mortar; charge flask with this mixture, and allow water to fall slowly upon it drop by drop.

$$H + I \rightarrow HI - 6000 \text{ cals.}$$

Experiment VII.—(Optional.) Use of Potassium Iodide to Determine Rate of Absorption from the Stomach.

Test the saliva for iodine by the iodide of starch test. Take, by mouth, a capsule containing 0.2 gram of KI or 10 drops of the saturated solution. Note the time. Test the saliva at end of each minute for iodine. If absorption is normal, a positive test should appear in fifteen minutes. Taking equal quantities of the iodide, the members of the class will be able to make a comparison of the rates of absorption. Determine the average rate of absorption of the individuals of the class who are fleshy; likewise calculate the average rate of those who are not fleshy. Your conclusions?

DERIVATIVES OF IODINE.

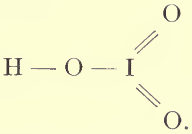
Oxygen.

Note.—Although iodine and ordinary oxygen do not combine with one another, O_3 reacts with iodine to form I_2O_5. Compare with conduct of fluorine.

Experiment VIII.—Preparation of Sodium Hypoiodite. Sodium Iodate.

These salts may be prepared by a method analogous to that used in the preparation of the corresponding salts of bromine and chlorine.

The hypoiodite, however, oxidizes quite readily, forming the iodate and iodide. If this mixture is treated with acid, iodic and hydriodic acids are liberated, but interact, liberating iodine. Recall the conduct of corresponding acids of bromine. The oxacids of iodine, HIO and HIO_3, are quite stable. Hydriodic acid:



Experiment IX.—Relative Affinity of Bromine and Iodine for Oxygen.

To 5 cm.³ of a solution of $KBrO_3$ add 5 cm.³ of dilute H_2SO_4. Divide the solution into two parts. To one portion add CS_2 and shake. Is the CS_2 colored? To the other portion add a very small flake of iodine; shake vigorously for two or three minutes; decant the clear solution into another test tube; add a few drops of CS_2; agitate the contents. Does the reddish-brown color indicate that iodine has a greater affinity than bromine for oxygen? Your reasons? (Examine structural formula of $HBrO_3$.)

Experiment X.—Properties of Iodates.

(*a*) Heat a few crystals of KIO_3 or $NaIO_3$ in a test tube and test for oxygen. Recall the preparation of oxygen from $KClO_3$. Equation?

(*b*) Pulverize .5 gram of KIO_3 or $NaIO_3$; mix thoroughly with .3 gram of powdered charcoal; place the mixture in a crucible and heat until the entire mass glows; cool; place crucible and contents in a beaker of hot water to dissolve the fused mass. Filter the solution. Devise a method to prove that an *iodide* was formed by the above reaction.

$$2NaIO_3 + 3C \longrightarrow 2NaI + \overline{3CO_2}.$$

(*c*) Place a small crystal of an iodate in a mortar with a little sulphur; rub the mixture vigorously with a pestle. Sharp explosions result from the friction. What other substance reacts like the iodate? Equations? Would you infer that iodates are strong oxidizers? Structural formula of $NaIO_3$?

Experiment XI.—Preparation of Iodic Acid.

Note.—Iodic acid may be prepared by a method analogous to the preparation of chloric acid, i.e., by the action of H_2SO_4 on a soluble iodate.

$$2NaIO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HIO_3.$$

The iodic acid may be crystallized out from the solution as a white solid.

The author has found the following method for the preparation of the acid to be very satisfactory: Place two or three small flakes of iodine in the bottom of the largest test tube among your apparata; add 15 cm.^{3} of strong HNO_3; take the mixture to the hood and boil vigorously until the solution becomes colorless. It may be necessary to add HNO_3 from time to time to oxidize all of the iodine. The colorless solution of HIO_3 should be boiled for sometime to concentrate it, and then set aside to allow crystals of the acid to form, or the solution may be tested at once as follows:

Add a few drops of HNO_3 to an $AgNO_3$ solution. Does a precipitate form? Repeat foregoing using a solution of KI instead of the HNO_3; observe the yellow color of the precipitate, AgI. Now add a few drops of the prepared solution supposed to contain iodic acid, to 3 cm.^{3} of the $AgNO_3$ solution. What is the color of the precipitate? Was it formed by the action of HNO_3? Your reasons?

$$4HNO_3 \rightarrow 2H_2O + \overline{4NO_2} + (O_2).$$
$$I_2 + H_2O + 5O \rightarrow 2HIO_3.$$

Save the iodic acid solution for the following experiment.

Experiment XII.—Oxidizing Action of Iodic Acid.

To 5 cm.^{3} of the solution of iodic acid add 2 cm.^{3} of CS_2; mix thoroughly. Note that the color of the CS_2 remains unchanged. Add a few drops of sulphurous acid, H_2SO_3 to the solution and then shake thoroughly. What is the substance which imparts the color to the CS_2? Has the odor of SO_2 disappeared?

$$2HIO_3 + 5H_2SO_3 \rightarrow 5H_2SO_4 + I_2 + H_2O.$$
$$HIO_3, Aq \rightarrow HI, Aq + 3O - 42{,}900 \text{ cal.}$$

Experiment XIII.—(L. T.) Periods of Induction in Chemical Reactions.

Instructions.—"There is a pleasing 'lecture experiment' for illustrating the 'period of induction.' A very dilute solution of H_2SO_3 and HIO_3 (1 gram, e.g., in 600 liters of water) is mixed with starch. The appearance of a visible blue color occupies a measurable time, which may be extended by using more dilute solutions."—Mellor's "Chemical Statics and Dynamics."

Experiment XIV.—Resemblance of the Properties of Corresponding Compounds of the Halogens.

(*a*) To a solution of $Pb(NO_3)_2$ add a few drops of a KCl solution; observe color of precipitate; filter. Determine solubility of precipitate in hot water. Repeat above using KBr. Also KI.

(*b*) Repeat (*a*) substituting $AgNO_3$ for $Pb(NO_3)_2$, and NH_4OH for hot water.

(*c*) Repeat (*b*) substituting $HgNO_3$ for $AgNO_3$.

Note the general similarity of conduct of the respective halides of each metal. Tabulate results.

Experiment XV.—Detection of Fluorides, Chlorides, Bromides and Iodides together in a Solution.

Devise a system of tests which will provide for the detection of the halogens in solution. Apply the system to a solution containing the four halides. Ask the assistant to give you an "unknown" solution; test for the presence of the halides. Report (?). Make a complete record of all work.

A general outline of the relations of the halogens is presented in the following table:

Physical Properties	Fluorine	Chlorine	Bromine	Iodine
Atomic weight	19	35.45	79.96	126.85
State or phase	Gas	Gas	Liquid	Solid
Color	Pale yellow	Greenish-yellow	Brown	Black
Specific gravity	1.15 (liquid)	1.15 (liquid)	3.18	4.96
Specific heat	<———	———	———	———<
Molecule of gas	F_2	Cl_2	Br_2	I_2(200°–600°)
Melting point	———	—102° (solid)	7.3°	114°
Boiling point	—186°	—33.7°	59°	184°
Chemical Properties				
Water decomposed	In the dark,	In the sunlight,	Slowly in the sunlight,	Only by indirect processes.
Formation of H-derivatives	Readily,	In the sunlight,	In heat of flame,	Only by indirect processes.
Heat of formation of H-derivatives	HF 37,600 cal.	HCl 22,000 cal.	HBr 8400 cal.	HI —6000 cal
Stability of H-derivatives	<———	———	———	———<
Affinity for oxygen	>———	———	———	———>
Oxides	None	Cl_2O, Cl_2O_3, ClO_2.	———	I_2O_5
Oxacids	None,	$HClO$	$HBrO$	———
∨		$HClO_2$	———	———
| *		$HClO_3$	$HBrO_3$	HIO_3
∨		$HClO_4$	$HBrO_4$	? HIO_4

* The stability of the oxacids and their corresponding salts increases with increase in oxygen-content.

It must be obvious to the student that the elements of this group or family are connected by properties, physical and chemical, which show a remarkable similarity. As a matter of fact, the uniformity is so marked that if the elements are arranged so as to show a gradation of any one property, the order will not be altered if they are arranged with respect to other properties. Again, these properties seem to bear so definite a relation to the atomic weight of an element, that it is now generally believed by chemists, although it is not yet fully proved, that *the properties of the elements*, as well as the properties of their compounds, *are periodic functions of their atomic weights.* For example, the specific heat of an element is inversely proportional to its atomic weight. These and other facts have led to the grouping of the elements into "natural families" or groups. The halogens are unique in the fact only that they represent the most prominent example of the gradation in properties observed among the members of a natural group of elements.

The regular, *periodic* variation in the properties of the elements constitutes what is known as the *periodic law*, by means of which the elements are given their natural classification. The law is illustrated by the following tables. (See Classification of the Elements.)

It should be noted before leaving this group that the halogen elements are, *par excellence*, acid elements; not only do their oxygen compounds, but their hydrogen compounds also exhibit acid properties.

CHAPTER XVI.

CLASSIFICATION OF THE ELEMENTS.

The classification of the elements into *metals*, *non-metals* and *metalloids* was made during the early development of chemistry when comparatively few elements were known. This classification was convenient, but it soon led to confusion, because elements were discovered which did not fall exclusively into any one of these three groups. It soon became evident to the chemists of that time that a new plan of classification was necessary; especially so after the announcement of the "Law of Multiple Proportion" by Dalton. As the result of the acceptance of this law, Prout (1815) promulgated the theory that the atomic weights of all the elements are exact multiples of the atomic weight of hydrogen, assuming that the atoms of other elements are merely condensations or aggregations of hydrogen atoms. The atomic weight determinations of Berzelius, Marignac and Stas did not prove that the atomic weights of the elements are exact multiples of the atomic weight of hydrogen.

Note.—"The work of T. W. Richards on the atomic weights of a large number of the metals should receive special attention. He has improved old methods, devised new ones and applied them with a skill which is rare. His determinations are to be ranked among the very best which have ever been made."—Jones' "Physical Chemistry."

The theory of Prout, though proven untenable, was instrumental in directing a great deal of attention to the question of atomic weights, with the result, that Döbereiner (1825) "on examining the atomic weights of correlated elements, observed that the atomic weight of the middle member of a group of three related elements was nearly a mean of the atomic weights of the other two elements. These groups of three were known as the "Triads of Döbereiner" and probably represent the first attempt to classify the elements on the basis of a relationship existing between properties and atomic weights. The student is referred to Venable's "Development of the Periodic Law."

NON-METALS.

Helium	Fluorine	Oxygen	Nitrogen	Carbon
Neon	Chlorine	Sulphur	Phosphorus	Silicon
Argon	Bromine	Selenium	Arsenic	Germanium*
Krypton	Iodine	Tellurium	Antimony*	Tin*
Xenon			Bismuth*	Boron
				(Aluminium)

* Metalloids.

METALS.

See table of elements for complete list of *metals*, *non-metals* and *metalloids*.

TRIADS OF DÖBEREINER (1825).

(Examples).

Lithium	Sodium	Potassium	
7	23	39	$\frac{7 + 39}{2} = 23$
Potassium	Rubidium	Cæsium	
39	85	133	$\frac{39 + 133}{2} = 86$
Calcium	Strontium	Barium	
40	88	137	$\frac{40 + 137}{2} = 88$
Sulphur	Selenium	Tellurium	
32	77	127	$\frac{32 + 127}{2} = 78$
Chlorine	Bromine	Iodine	
35	80	126	$\frac{35 + 126}{2} = 80$

"LAW OF OCTAVES."

(Newland's, 1864.)

						Co. &								Pt. &	
H.	1	F.	8	Cl.	15	Ni.	22	Br.	29	Pd.	36	I.	42	Ir.	50
Li.	2	Na.	9	K.	16	Cu.	23	Rb.	30	Ag.	37	Cl.	44	Tl.	53
G.	3	Mg.	10	Ca.	17	Zn.	24	Sr.	31	Cd.	38	Ba. &V.	45	Pb.	54
Bo.	4	Al.	11	Cr.	18	Y.	25	Ce. & La.	32	U.	40	Ta.	46	Th.	56
C.	5	Si.	12	Ti.	19	In.	26	Zr.	33	Sn.	39	W.	47	Hg.	52
N.	6	P.	13	Mn.	20	As.	27	Di. & Mo.	34	Sb.	41	Nb.	48	Bi.	55
O.	7	S.	14	Fe.	21	Se.	28	Ro. & Ru.	35	Te.	43	Au.	49	Os.	51

MENDELEEF'S ORIGINAL TABLE (1869)

(LIEB. ANN. SUPPL. 8, 133, 1874).

Series	Group I. — R_2O.	Group II. — RO.	Group III. — R_2O_3.	Group IV. RH_4, RO_2.	Group V. RH_3, R_2O_5.	Group VI. RH_2, RO_3.	Group VII. RH, R_2O_7.	Group VIII. — RO_4.
1	H=1							
2	Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
4	K=39	Ca=40	—=44	Ti=48.1	V=51	Cr=52	Mn=55	Fe=56, Ni=58 Co=59, Cu=63
5	(Cu)=63	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	Y=88	Zr=90	Cb=94	Mo=96	—=100	Rh=103, Ru=103.8 Pd=108, Ag=107.9
7	(Ag)=108	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	Li=138	Ce=140	—	—	—	— —
9	(—)	—	—	—	—	—	—	— —
10	—	—	Er=178	La=180	Ta=182	W=184	—	Ir=193.1, Pt=194.8 Os=200, Au=196.7
11	(Au)=199	Hg=200	Ti=204	Pb=207	Bi=208	—	—	— —
12	—	—	—	Th=231	—	U=240	—	— —

NATURAL CLASSIFICATION. (Lothar Meyer, 1870).

Hydrogen, H = 1.008							
I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Li = 7.03	Be = 9	B = 11	C = 12	N = 14.01	O = 16	F = 19	
Na = 23.05	Mg = 24.36	Al = 27.1	Si = 28.4	P = 31	S = 32.06	Cl = 35.45	
K = 39.15	Ca = 40.1	Sc = 44.1	Ti = 48.1	V. = 51.2	Cr = 52.1	Mn = 55	Fe = 55.9, Co = 59, Ni = 58.7
Cu = 63.6	Zn = 65.4	Ga = 70	Ge = 72.5	As = 75	Se = 79.2	Br = 79.96	
Rb, 85.4	Sr, 87.6	Y, 89	Zr, 90.7	Cb, 94	Mo, 96	—	Ru, 101.7, Rh, 103, Pd, 106
Ag = 107.93	Cd = 112.4	In = 115	Sn = 119	Sb = 120.2	Te = 127.6	I = 126.97	
Cs = 132.9	Ba = 137.4	La = 138.9	Ce = 140.25	(Pr = 140.5 Nd = 143 6)	—	Sa = 150	— — —
—	—	—	—	—	—	—	
—	Er = 166	Yb = 173	—	Ta = 183	W = 184	—	Os = 191, Ir = 193, Pt = 194.8
Au = 197.2	Hg = 200	Tl, 204.1	Pb = 206.9	Bi = 208			
	Rd = 225	—	Th = 232.5	—	U, 238.5	—	— — —
R_2O	R_2O_2	R_2O_3	R_2O_4 $R H_4$	R_2O_5 $R H_3$	R_2O_6 $R H_2$	R_2O_7 $R H$	$(R O_4)$

PERIODIC ARRANGEMENT.

Table I.

	Group O. (Inert Gases).	Group I.		Group II.		Group III.		Group IV.		Group V.		Group VI.		Group VII.		Transition Elements
		M	m	M	m	M	m	M	m	M	m	M	m	M	m	
1st short, or typical, period.....	H = 1.008 He = 4	Li = 7		Be = 9			B 11		C 12		N 14		O 16		F 19	
2nd short perioid..............	Ne = 20	Na = 23		Mg = 24.4			Al 27		Si 28.4		P 31		S 32		Cl 35.5	
1st long period even series .... odd “	A = 39.9	K = 93	Cu 63.6	Ca = 40	Zn 65.4	Sc = 44	Ga 70	Ti = 48	Ge 72.5	V = 51	As 75	Cr = 52	Se 79.2	Mn = 55	Br 80	Fe = 55.9 Ni = 58.7 Co = 59
2nd long period even series .... odd “	Kr = 87.8	Rb = 85.4	Ag 107.93	Sr = 87.6	Cd 112.4	Y = 89	In 115	Zr = 90.6	Sn 119	Cb = 94	Sb 120	Mo = 96	Te 127.6	? = 100	I 127	Ru = 101.7 Rh = 103 Pd = 106.5
3rd long period even series .... odd “	X = 128	Cs = 133	—	Ba = 137.4	—	La = 139	Gd 156	Ce = 140.2	—	Pr = 140.5 ?	—	Nd = 143.6 ?	—	Sa = 150 ?	—	? = 152 ? = 153 ? = 154
4th long period even series .... odd “		—	Au 197	Er = 166?	Hg 200	Yb = 173	Tl 204	—	Pb 207	Ta = 181	Bi 208.5	W = 184	— 214.0	—	— 219.0	Os = 191 Ir = 193 Pt = 195
5th long period even series .... odd “		—	—	Rd = 225?	—	? = 230	—	Th = 232.5	—	—	—	U = 238.5	—	? = 240	—	— — —
Oxygen compounds............	—	R_2O		R_2O_2		R_2O_3		R_2O_4		R_2O_5		R_2O_6		R_2O_7		(RO_4)
Hydrogen compounds..........	—	—		—		—		RH_4		RH_3		RH_2		RH		

Atomic weights are given in round numbers. Some of the very rare elements have been omitted from the table.

PERIODIC ARRANGEMENT.

TABLE II.

Short Periods.

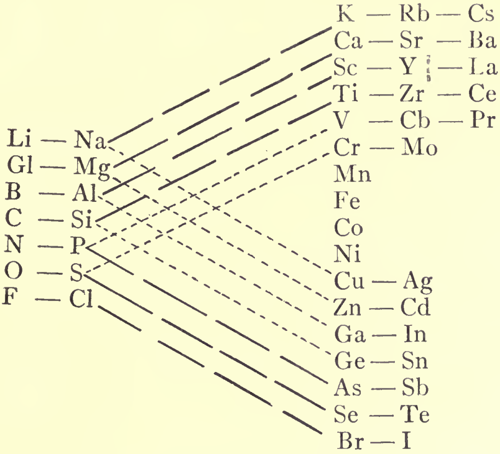
1	2	3	4	5	6	7
Li	**Be**	**B**	**C**	**N**	**O**	**F**
7·03	9	11	12	14·01	16	19
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
23·05	24·36	27·1	28·4	31	32·06	35·45

Long Periods of seventeen each.

K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**
39·15	40·1	44·1	48·1	51·2	52·1	55	55·9	59	58·7	63·6	65·4	70	72·5	75	79·2	79·95
Rb	**Sr**	**Y**	**Zr**	**Cb**	**Mo**	—	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**
85·5	87·6	89	90·6	94	96		101·7	103	106·5	107·93	112·4	115	119	120·2	127·6	126·97
Cs	**Ba**	**La**	**Ce**	**Pr**	**Nd**	—	—	—	—	—	—	—	—	—	—	—
132·9	137·4	138·9	140·25	140·5	143·6											
—	**Er?**	**Yb**	—	**Ta**	**W**	—	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	—	—
	166	173		181	184		191	193	194·8	197·2	200	204·1	206·9	208		
—	**Rd**	—	**Th**	—	**U**	—	—	—	—	—	—	—	—	—	—	—
	225		232·5		238·5											
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17

The inert gases of the atmosphere and the very rare elements have been omitted from this table. (H = 1.008.) International atomic weights (1908).—Jour. Amer. Chem. Soc.

Many attempts have been made to so modify the form of the foregoing tables that the position of an element will more faithfully represent its relationships. The following is an example:



BAYLEY'S TABLE.

The following tabulated data may serve to make more significant the relative positions of the elements in the periodic table:

Specific Gravity.

Na	Mg	Al	Si	P	S	Cl
.97	1.7	2.5	2.4	2.2	2.0	1.3

K.	Ca	Sc	Ti	V.	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
.87	1.6	3.8	4.?	5.5	6.8	7.2	7.9	8.5	8.9	8.9	7.2	5.9	5.5	5.6	4.8	3.2.

ATOMIC VOLUME.

$$V = \frac{\text{At. Wt.}}{D}$$

Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
23.7	13.8	10.6	10.7	12.8	16.	26.

K	**Ca**	**Se**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**
45.4	25.3	?	12.5?	9.2	7.65	7.6	7.0	6.8	6.3	7.1	9.4	11.5	12.?	13.1	16.5	25.

SPECIFIC HEAT.

Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
.29	.245	.20	.16	.19	.18	(Gas)

K	**Ca**	**Se**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**
.166	.170	.153	—	—	.121	.122	.112	.107	.108	.093	.093	.079	—	.082	.08	.084

VALENCE.

			C, H_4	N, H_3	O, H_2	Fl, H
			Si, H_4	P, H_3	S, H_2	Cl, H
Li, Cl	Be, Cl_2	B, Cl_3	C, Cl_4	N, Cl_3	O, Cl_2	Fl, F
Na, Cl	Mg, Cl_2	Al, Cl_3	Si, Cl_4	P, Cl_3	S, Cl_2	Cl, Cl
Na_2, O	Mg, O	Al_2, O_3	Si, O_2	P_2, O_5	S, O_3	Cl_2, O_7
Na, OH	Mg, $(OH)_2$	Al, $(OH)_3$	Si, $(OH)_4$	P, $(OH)_5$	S, $(OH)_6$	Cl, $(OH)_7$

ATOMIC VOLUME—SPECIFIC GRAVITY.

Element.	Atomic Weight.	Specific Gravity.*	Atomic Volume.*	Element.	Atomic Weight.	Specific Gravity.	Atomic Volume.	Element.	Atomic Weight.	Specific Gravity.	Atomic Volume.
Li	7.0	0.59	11.9	S	32.0	2.05	16.	Cu	63.6	8.9	7.13
Be	9.0	2.07	4.4	Cl	35.4	Gas	26.	Zn	65.4	7.2	9.37
B	11.0	2.5	4.1	K	39.0	0.87	45.4	Ga	70.0	5.9	11.5
C	12.0	3.5	3.4	Ca	40.0	1.58	25.3	As	75.	5.6	13.1
N	14.0	Gas		Sc	44.0	3.8?		Se	79.0	4.8	16.5
O	16.0	Gas		Ti	48.0	4.?	12.5?	Br	79.9	3.19	25.
F	19.0	?		V	51.2	5.5	9.3	Rb	85.5	1.52	56.3
Na	23.0	0.97	23.7	Cr	52.0	6.8	7.65	Sr	87.6	2.5	34.4
Mg	24.0	1.74	13.8	Mn	5.50	7.14	7.6	Ag	107.9	10.6	10.2
Al	27.0	2.60	10.6	Fe	55.9	7.86	6.9	I	126.9	4.95	25.6
Si	28.0	2.39	10.7	Ni	58.7	8.90	6.31	Te	127.6	6.25	20.4
P	31.0	2.20	12.8	Co	59.0	8.5	6.82	Cs	132.9	1.9	70.

*Huth's, Das periodische Gesetz der Atomgewichte.

EXERCISES.

1. Draw a *periodic curve* of the elements named in the above table, tabulating the specific gravities on the vertical axis, and the atomic weights on the horizontal axis.
2. Repeat (1), substituting atomic volumes for specific gravities.
3. Repeat (1), substituting specific heats (see Appendix) for specific gravities.

CHAPTER XVII.

OXYGEN FAMILY.

Oxygen,	O,	16.00,
Sulphur,	S,	32.06,
Selenium,	Se,	79.2,
Tellurium,	Te,	127.6.

It has been pointed out in the preceding chapter that the chemical and physical properties of the elements bear a definite relation to their atomic weights. The student should note carefully the conduct of these four elements whose atomic weights place them in the same "natural group," to ascertain whether they conform to this so-called "periodic law."

OXYGEN, O.

At. Wt. 16. Mol. Wt. 32.

Preparation and Properties of Oxygen.

Experiment I.—Recall the previous experiments with oxygen. Fix in mind the physical and chemical properties of the elementary substance.

Hydrogen Derivatives.

Experiment II.—Recall experiments suggested by the following equations:

$$H_2 + O \rightarrow H_2O,\ Aq + 68{,}360 \text{ cals.}$$
$$H_2 + O_2 \rightarrow H_2O_2,\ Aq + 45{,}300 \text{ cals.}$$

Experiment III.—Oxidizing Action of Hydrogen Dioxide.

Place 5 cm.^{3} of lead acetate in an evaporating dish; moisten a strip of writing paper with the solution, then hold the paper in a current of hydrogen sulphide. Results? Allow the paper to dry. Place 2 cm.^{3} of H_2O_2 in a test tube; using a glass rod wet with the H_2O_2, write your name upon the paper. Explain.

Oxygen Derivatives.

Experiment IV.—Recall the formation of ozone.

$$O_2 + O \rightarrow O_3 - 32{,}400 \text{ cals.}$$

SULPHUR, S.

At. Wt. 32.06 Mol. Wt., (S_2, S_4, S_6, S_8).

Properties of Sulphur.

Experiment I.—Transition Points. Plastic Sulphur.

Procure a few grams of roll sulphur; note its color, taste, odor, relative density, structure, luster. Place 5–10 grams of the sulphur in a dry test tube; heat gently, observing the yellow deposit of sulphur (flowers of sulphur) on the cooler portions of the tube as the experiment proceeds; increase the temperature of the tube until the sulphur melts. Determine the melting point by means of the thermometer, then remove it; continue to increase the supply of heat, noting the change in color of the fluid. At 160°–260° the yellow mobile fluid changes to a dark liquid so viscous that the test tube may be inverted without spilling the sulphur. Heat to boiling (448.5°); observe that the fluid becomes less viscous. Collect a portion of the sulphur vapor in a cold flask or bottle.

Pour the boiling sulphur from the test tube into a beaker of water. Examine the cooled mass. Does it resemble roll sulphur? Is it amorphous or crystalline? It is known as *plastic sulphur.* Place a part of it on a watch glass and set aside to be examined after a couple of days. Results? Reserve the other portion for the following experiment.

Note.—Plastic (elastic) sulphur and, in fact, all amorphous bodies are spoken of as "supercooled liquids." See Lecture Notes.

Experiment II.—Monoclinic Sulphur.

Melt 25–50 grams of sulphur in a porcelain evaporating dish or a Hessian crucible; cool until a crust has barely formed over the surface; perforate the crust with a glass rod, and pour off the liquid portion. The sides and bottom of the dish will be covered with *transparent*, needle-like crystals of sulphur. Set the *monoclinic* crystals aside for several days, then observe that they have become opaque like roll sulphur.

Experiment III.—Rhombic Sulphur. Solubility of the Allotropic Forms of Sulphur.

(*a*) Place a small piece of roll sulphur in the bottom of a test tube; add 5 or 6 $cm.^3$ of CS_2; after shaking for some time, pour a $cm.^3$ of the liquid upon a glass plate; the CS_2 will evaporate spontaneously depositing crystals of rhombic (octahedral) sulphur. Examine the crystals with a hand-magnifying glass or by the aid of a microscope. Are the crystals soluble in H_2O? In CS_2?

(*b*) Repeat (*a*) using plastic amorphous sulphur, monoclinic (prismatic) sulphur, and flowers of sulphur. Test each form separately. Record results. Sulphur crystallizes in how many forms? Such a substance is given what name?

Native **sulphur** is a yellow crystalline substance composed largely of partially formed rhombic crystals. It has a sp. gr. of 2.06; melts at 114.5°, and boils at 448.5°. Below 96°, prismatic or monoclinic sulphur is unstable and passes into the rhombic variety; above 96° rhombic sulphur is unstable and passes into the monoclinic. The range of stable rhombic sulphur extends from low temperature to 96° C.; that of monoclinic from 96° to 119.5°, its melting-point. Amorphous sulphur, likewise monoclinic, if allowed to stand at ordinary temperatures becomes hard and brittle; it passes into the rhombic.

That which is of special interest is the fact that monoclinic sulphur with a sp. gr. of 1.96 and a melting-point of 119.5°, possesses properties quite different from those possessed by the rhombic form. (The opaqueness which was attendant upon the transformation of the monoclinic into rhombic crystals, is due to the fact that the rhombic crystals with their greater sp. gr. (2.07) occupy less actual space than the monoclinic or prismatic.) The difference between these two varieties of sulphur suggests that which was observed between the two forms of oxygen, namely, ordinary oxygen and ozone. (Monoclinic sulphur is frequently referred to as the analogue of ozone.) It is quite doubtful, however, whether an analogous explanation will satisfactorily meet the requirements of both cases. It seems quite certain in the case of sulphur that the different energy contents of the two forms are in some way intimately related to the difference in properties. The change from the monoclinic to the rhombic form is accompanied by an evolution of a considerable amount of heat. (Compare ozone.) It is evident that the molecule of monoclinic sulphur contains more internal energy than the molecule of rhombic sulphur. Favre and Silbermann (Ann. Chim. Phys.) treated this, and found the following:

$$\begin{aligned} &S(\text{monoclinic}) + O_2 \longrightarrow \overline{SO}_2 + 73{,}300 \text{ cal.} \\ &S(\text{rhombic}) \quad\;\; + O_2 \longrightarrow \overline{SO}_2 + 71{,}000 \text{ cal.} \end{aligned}$$

The difference, 2300 cal., is the thermal equivalent of the difference between the energy contents of the two forms of sulphur.

Experiment IV.—Union of Sulphur with Metals to Form Sulphides.

Place a small globule of mercury in a clean mortar containing a little sulphur; rub the two substances together by use of pestle. What is the color of the resulting powder? Compare it with the mercury sulphide found on the end-shelf.

With the exception of platinum and gold, finely divided metals when rubbed with sulphur combine with the latter to form sulphides.

Experiment V.—Formation of Ferrous Sulphide. Hydrogen Sulphide.

To 5 grams of powdered sulphur in a mortar, add 7 grams of fine iron filings; mix thoroughly and introduce mixture into a small test tube; heat the tube until the contents glow; cool, and break the tube; examine the fused mass. Is it a mixture or a compound? To several small pieces in a test tube, add dilute HCl or H_2SO_4. Note the odor of the evolved gas, hydrogen sulphide or, as it is sometimes styled, sulphuretted hydrogen. Indicate the chemical reactions by means of equations.

$$H_2 + S \text{ (rhombic)} \rightarrow H_2S + 2730 \text{ cals.}$$

Experiment VI.—Preparation and Properties of Hydrogen Sulphide. Hydrosulphuric Acid.

Place several pieces of ferrous sulphide (iron sulphide) in the flask of the apparatus used for generating hydrogen; insert the stopper; through the thistle tube introduce 2 cm.^{3} of strong HCl or H_2SO_4. Observe the slow evolution of the hydrogen sulphide, H_2S; add H_2O slowly until the evolution of gas becomes rapid. Explain action of H_2O. Collect some of the gas over water. Note its color, odor and its density as compared with air. Inflame a bottle of the gas. Explain the deposit on the inside of the test tube.

Determine the solubility of the gas in water. Test the action of an aqueous solution of it upon litmus paper, and a solution of sodium carbonate. A water solution of H_2S is frequently termed *hydrosulphuric acid* or *sulphrydic acid.*

Raise the delivery tube from the water; attach a jet and ignite the issuing gas if all the air has been expelled from the flask. Hold a cold piece of porcelain—for example, an evaporating dish or a mortar—in the darker portion of the flame. What substance, evidently in the free state in the inner portion of the flame, is deposited upon the porcelain? What other elementary substance probably exists in a free state in the interior of the flame? State the probable reason for the existence in the free state of these two elementary substances.

Note.—Use the remaining gas to saturate 50 cm.^{3} of H_2O in a flask. This aqueous solution may be used for the following experiments if the laboratory is not equipped with a generator which furnishes a constant supply of H_2S.

$$(H_2S. Aq) = 4500 \text{ cal.}$$

Experiment VII.—Properties of Hydrogen Sulphide.—Continued.

(*a*) Instability of hydrogen sulphide. In a clean test tube expose an aqueous solution of the gas to the action of the air for several days. Results? Equation?

(*b*) Reducing action of hydrogen sulphide. Pass a stream of H_2S through 5 cm.^{3} of strong H_2SO_4 until there is evidence that SO_2 is being evolved and free sulphur is deposited. Equation? Could H_2SO_4 be used to dry H_2S?

To 5 cm.^{3} of a $K_2Cr_2O_7$ (potassium dichromate) solution add 2 cm.^{3} of HCl. What is the color of the solution? Pass H_2S through the solution until its color is green, due to the presence of $CrCl_3$. Is free sulphur deposited? Write the structural formula for $K_2Cr_2O_7$. What is the valence of the chromium in this salt? Structural formula for $CrCl_3$? Valence of chromium in this salt? Write equations showing nature of the reactions.

The above may be repeated using $KMnO_4$ instead of $K_2Cr_2O_7$.

To 3 cm.^{3} of ferric chloride, $FeCl_3$ add a few drops of potassium ferricyanide, $K_3Fe(CN)_6$. Note the color. Repeat, using ferrous sulphate, $FeSO_4$, instead of $FeCl_3$. Note the color. Pass H_2S through separate solutions of $FeCl_3$, and $FeSO_4$, for two or three minutes; filter and test each filtrate with $K_3Fe(CN)_6$. Explain results. Equations?

(*c*) Formation of sulphides. Allow hydrogen sulphide to come into contact with a moist silver coin. Results? Equation?

(*d*) Determine the electrical conductivity of an aqueous solution of H_2S. What is your conclusion as to its degree of dissociation? Is it a strong or weak acid? Why?

Experiment VIII.—Hydrogen Sulphide and Sulphides.

Introduce 3 cm.^{3} of $ZnSO_4$ solution into a test tube add 5 cm.^{3} of water. Test the solution with litmus paper. Is the solution neutral? Saturate solution with H_2S. Does a precipitate of ZnS form? Is the precipitate soluble in HCl? Test by adding 2 cm.^{3} of said acid. Saturate solution a second time with the H_2S. Is a precipitate formed? Write the equations for the above reactions showing the interaction of the ions.

Repeat the foregoing, using solutions of $CuSO_4$, $Cd(NO_3)_2$, NaCl, $MnSO_4$, $BaCl_2$, H_3AsO_3, in place of $ZnSO_4$. Classify the sulphides according to their solubility in water, dilute acids and strong acids.

Sulphides of the alkalies and the alkaline earths are soluble in water; all other metallic sulphides are insoluble. The behavior of the insoluble sulphides towards acids may be summarized as follows:

(*a*) Sulphides decomposed by dilute acids like HCl or H_2SO_4. Examples: FeS, ZnS, MnS.

(*b*) Sulphides not decomposed by dilute acids, but soluble in warm strong HCl. Examples: PbS, Sb_2S_3, SnS, NiS, CoS.

(*c*) Sulphides not soluble in strong HCl, but are decomposed by *aqua regia* or by a mixture of HCl and $KClO_3$. Examples: HgS, As_2S_3.

Experiment IX.—A Test for Sulphides.

(*a*) When soluble sulphides are decomposed by acids, H_2S is evolved. The presence of the gas may be detected (1) by its odor; (2) by its action upon lead acetate. This latter test is usually made as follows: A piece of filter paper moistened with lead acetate is held over the mouth of the test tube in which the reaction occurs. The H_2S causes a black stain due to the formation of lead sulphide.

(*b*) Prepare a dilute solution of Na_2S or K_2S. Note that the odor of H_2S is not present. Following (*a*), test for sulphides. Equations?

Experiment X.—Optional. Polysulphides. Hydrogen Polysulphide.

(*a*) To 20 cm.^{3} of a solution of a soluble sulphide, e.g., Na_2S, add a pinch of pulverized sulphur; shake vigorously until the color of the solution becomes reddish-yellow. After evaporation of the solution, the substances remaining have a composition varying from Na_2S_2 to Na_2S_5. Dissolve the residue in water. Divide the solution into two parts. To one portion add strong HCl and note the liberation of H_2S and free sulphur (rhombic). Add the other portion *to* 3 cm.^{3} of strong HCl. Observe that no H_2S is evolved, but that a heavy yellow oil, hydrogen pentasulphide (H_2S_5) forms a distinct phase in the bottom of the tube. H_2S_5 is unstable in the presence of moisture and decomposes into H_2S and S.

(*b*) Add a solution of CaS_2, (CaS_x) to HCl; the yellow oily liquid, hydrogen polysulphide, separates.

Oxygen Derivatives of Sulphur.

Experiment XI.—Formation of Sulphur Dioxide.

(*a*) Oxidation of sulphur by burning in the air. Set fire to a few small pieces of sulphur upon the inverted cover of a porcelain crucible. Observe the color of the flame and note the odor of the sulphur dioxide, SO_2, fumes.

(*b*) Roasting a pyrite, FeS_2. Heat 1 gram of granular pyrite in a hard glass test tube. Observe the deposit of sulphur on the cooler portions of the tube,and notice the odor of evolved SO_2. What is the effect of heating those portions of the tube on which sulphur is deposited?

(*c*) Reduction of H_2SO_4 by sulphur. Heat a small piece of roll sulphur with strong H_2SO_4 in a test tube. Wave the escaping fumes toward the nose. Odor? Equation? Pieces of charcoal may be substituted for the sulphur, and the above procedure followed.

(*d*) Reduction of H_2SO_4 by copper. See Exp. XII.

$$S + O_2 \rightarrow SO_2 + 71{,}000 \text{ cal.}$$

Would you infer from equation that SO_2 is a stable or an unstable compound?

Experiment XII.—(Hood) Laboratory Preparation of Sulphur Dioxide.

Fit a 300 cm.^{3} flask with a rubber stopper provided with thistle tube and a delivery tube, and add two or three small bunches of copper shavings or 10 grams of granulated copper; support the flask in ring stand upon a wire gauze; connect flask (Fig. 29) with wash bottle, one-third filled with strong H_2SO_4; the wash bottle should be provided with a doubly bent delivery tube, reaching almost to the desk-top. Add through thistle tube 100 cm.^{3} to 150 cm.^{3} of strong H_2SO_4; heat bottom of flask gently until there is a brisk evolution of gas. Identify the gas. Fill three bottles with the gas by downward displacement of air; stopper the bottles. Saturate 25 cm.^{3} of H_2O with the gas; the delivery tube should be placed

1 cm. above the surface of the water. What evidence is there that the gas is dissolving? Proceed with the study of the properties of SO_2. Equation indicating action of strong H_2SO_4 on Cu?

Experiment XIII.—Properties of Sulphur Dioxide.

(*a*) Bleaching properties of sulphur dioxide. Place a moist strip of colored calico and the moistened petals of a red flower in one bottle of the gas. Set them aside until the close of the laboratory period. Effect of gas?

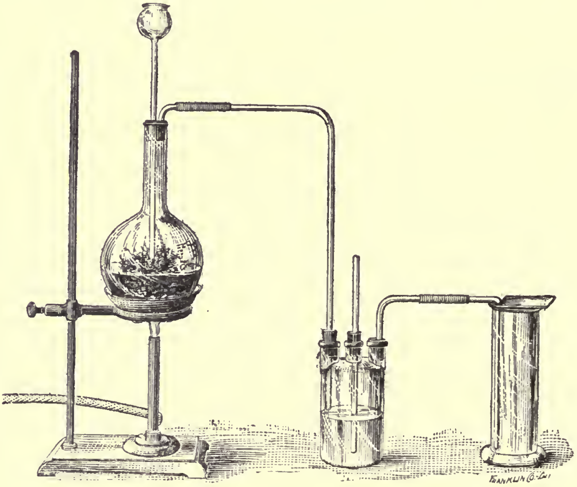


FIG. 29.

(*b*) Using another bottle of the gas, ascertain if SO_2 will burn or support combustion. Conclusions?

(*c*) Devise a method for determining the density of SO_2 as compared with air. Record procedure and results.

(*d*) What is the effect of dry SO_2 upon dry blue litmus paper?

Experiment XIV.—Optional. Liquid Sulphur Dioxide.

Note.—The critical temperature of SO_2 is 156° C. The gas, SO_2, when cooled to the temperature of a freezing mixture of salt and ice, condenses to a liquid which boils at about —8° C.

Pass a slow current of dry SO_2 through a long spinal tube, immersed in a freezing mixture, into a U-tube, the arms of which are provided with glass stop cocks. This latter tube, "sulphur dioxide condenser," must also be placed in a freezing mixture. The liquid SO_2 may be kept indefinitely in the closed tube. When gaseous SO_2 is required, one of the stop cocks is opened.

Experiment XV.—Aqueous Solution of Sulphur Dioxide. Sulphurous Acid.

Test the action of the aqueous solution of SO_2 prepared in Exp. XII. upon blue litmus paper. To 1 cm.³ of the solution add 10 cm.³ of H_2O. Taste a drop of the solution. Does the solution manifest the properties of an acid, base or salt? Explain its formation. Equation? Heat 5 cm.³ of the acid solution. Note the odor of the fumes. SO_2 is the anhydride of what acid? What is the significance of the *ous* ending? What is the termination of its corresponding salts? Write the structural formula of sulphurous acid. How many series of salts can H_2SO_3 form? What name is applied to such acids? Would you say that H_2SO_3 is a very stable compound? Why?

$$SO_2 + H_2O \rightarrow SO_2, Aq + 7{,}700 \text{ cal.}$$

Experiment XVI.—Preparation of a Soluble Sulphite. Action of Strong Acids Upon Soluble Sulphites. Test for Sulphites.

Place 10 cm.³ of H_2SO_3 in a test tube; add a solution of NaOH until the odor of SO_2 has disappeared. Divide the sodium sulphite solution into two parts. To one portion add a little HCl; to the other portion add H_2SO_4. Is SO_2 evolved in both cases? Equations?

Experiment XVII.—A Test for Sulphites. Reversible Reaction.

To 5 cm.³ of a $BaCl_2$ solution add drop by drop several cm.$_3$ of H_2SO_3. Observe that the white precipitate of $BaSO_3$ is not heavy. Write the equation for the reaction. Is the precipitate soluble in HCl? What acid was formed when $BaSO_3$ was precipitated? Will this acid have a tendency to reverse the action of the H_2SO_3? Is it probable that the precipitation of $BaSO_3$ would be more complete if the acid were removed as fast as it formed?

Ascertain the effect of adding a solution of sodium or potassium acetate to a solution of $BaCl_3$ to which has been added H_2SO_3. Is the precipitation more complete? Is the precipitate soluble in HCl? What gas is evolved? Explain the further precipitation of $BaSO_3$ on the addition of sodium acetate, $NaC_2H_3O_2$, by use of "ionic" equations.

All sulphites except those of the alkali metals are insoluble in water. Dilute acids decompose all sulphites with an evolution of SO_2. The larger number of the sulphites are converted into sulphides and sulphates when heated. Those of the alkaline earths yield a metallic oxide and SO_2.

$$4Na_2SO_3 \rightarrow Na_2S + 3Na_2SO_4,$$
$$BaSO_3 \rightarrow BaO + SO_2.$$

Experiment XVIII.—Reducing Action of Sulphurous Acid.

(*a*) What is the effect of adding H_2SO_3 to a very dilute solution of $KMnO_4$ acidulated with H_2SO_4? Equations?

(*b*) Substituting $K_2Cr_2O_7$ for $KMnO_4$, repeat (*a*). Equations?

(*c*) Recall action of H_2SO_3 on HIO_3. Was reduction accompanied by oxidation? Explain.

Sulphurous acid in the presence of more powerful *reducing* agents may act as an oxidizing substance as follows:

Experiment XIX.—Oxidizing Action of Sulphurous Acid.

(*a*) Add 2 cm.^{3} of HCl to 5 cm.^{3} of $SnCl_2$; add 2 cm.^{3} of H_2SO_3; warm gently; observe the formation of a yellow precipitate of SnS_2. As the reactions usually proceed rather slowly, allow the test tube and contents to remain undisturbed for 10 minutes to 15 minutes. The H_2SO_3 is reduced to H_2S, and the $SnCl_2$ is oxidized to $SnCl_4$.

$$(1)\quad 3SnCl_2 + 6HCl + H_2SO_3 \rightarrow 3SnCl_4 + 3H_2O + \overline{H_2S}.$$
$$(2)\quad SnCl_4 + 2H_2S \rightarrow SnS_2 + 4HCl.$$

(*b*) Nascent hydrogen reduces sulphurous acid. Place a piece of granulated zinc in the bottom of a test tube; add a little dilute HCl; add a few drops of H_2SO_3. Test for the presence of H_2S by holding a piece of filter paper moistened with a drop of lead acetate over the mouth of the tube (?). Equations?

Experiment XX.—Oxidation of Sulphurous Acid. Sulphuric Acid.

(*a*) To 3 cm.^{3} of H_2SO_3 add a little H_2O_2; shake, then add a small quantity of a $BaCl_2$ solution. Is the precipitate which forms soluble in HCl? Recall the solubility of $BaSO_3$ in HCl. The white precipitate insoluble in HCl is $BaSO_4$. What acid was evidently present in the solution before the $BaCl_2$ was introduced? Explain its formation. Equations? Using H_2SO_4 from the reagent shelf, test its action on $BaCl_2$. Is the precipitate soluble in HCl? How can you distinguish between a sulphite and a sulphate?

(*b*) Repeat (*a*) using "bromine water." Results? Equations?

(*c*) Slow oxidation of H_2SO_3 by oxygen of the air. Expose 10 cm.^{3} of H_2SO_3 to the action of the air for several hours. Test it with $BaCl_2$. Was $BaSO_3$ or $BaSO_4$ formed? Give reasons for answer. Equations?

(*b*) Rapid oxidation of H_2SO_3 by oxygen of the air by use of a catalyser, N_2O_3. Prepare the gaseous catalyser, N_2O_3, as follows: Put 10 or 15 grams of granulated copper or a bunch of copper shavings in a generating flask; add sufficient water through the thistle-tube to cover the lower end of the latter; then introduce 20 cm.^{3} of concentrated HNO_3. Observe the formation of a reddish-brown gas which is a mixture of N_2O_3 and N_2O_4. The colorless gas, NO, is the initial product formed by the action of HNO_3 on copper, but in the presence of air, it quickly oxidizes to the above-mentioned gases. Fill a small flask with NO by displacement of water; allow air to enter flask that N_2O_3 may be formed, then pour 2 cm.^{3} of H_2SO_3 into the flask; fit a stopper in place and shake.

Observe that the color disappears. Remove stopper until gas is again colored; insert stopper and shake (?). Repeat this operation several times, then by use of $BaCl_2$ and HCl prove the presence of H_2SO_4.

Experiment XXI.—(L. T.) The Manufacture of Sulphuric Acid.—Chamber Process.

The purpose of the following experiment is to acquaint the student with the "chemistry" of the sulphuric acid industry. References and lectures should supplement the experiment. A flask or glass globe of two or three liters' capacity is fitted with a cork through which passes five delivery tubes reaching to the center of the flask (Fig. 30). The middle tube *e* serves as an escape for the excess of gases introduced through the other tubes. Through a tube *d* air can be forced into the flask (chamber) by a bellows or a bicycle pump. The other three tubes are connected by glass tubing with separate generating flasks *a*, *b* and *c*. *a* is the flask in which SO_2 is prepared by heating copper shavings and concentrated H_2SO_4. (The SO_2 may be prepared by heating granular pyrite in a boat placed in hard glass tubing. A current of air should be drawn through the tube over the pyrite by use of an aspirating bottle.) Nitric oxide, N_2O_2, which in the presence of oxygen oxidizes to N_2O_3, the catalyser, is generated in *b* by the action of dilute HNO_3 on copper shavings. (Nitric acid vapor may be used instead.) Steam, H_2O, is supplied by boiling water in flask *c*. If the products (gases) from *a* and *b* together with air are introduced without a sufficient supply of steam, a frost-like

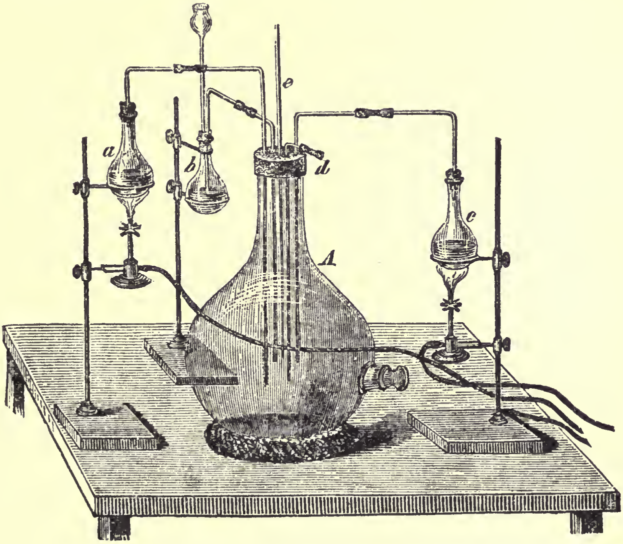
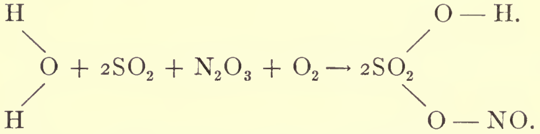
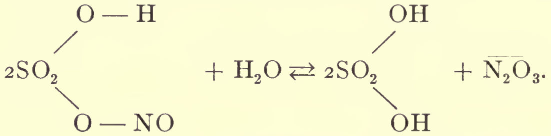


FIG. 30.

deposition of nitrosyl-sulphuric acid crystals is observed upon the walls of the flask.



Now increase the supply of steam and note the disappearance of the crystals and the formation of a heavy oily fluid:



When 10 cm.^{3} to 15 cm.^{3} of liquid have collected in the flask, the experiment may be interrupted. Place the liquid in a test tube and reserve it for following experiments.

Experiment XXII.—Properties of Sulphuric Acid (Hydrogen Sulphate).

(*a*) Dehydrating action of sulphuric acid. Action of sulphuric acid with organic matter. Remove the head of a match; dip the wood into hot concentrated H_2SO_4. Results? Write your name with dilute H_2SO_4 upon a piece of paper. Dry the paper. Results?

To a little sugar in the bottom of a test tube add strong H_2SO_4; heat gently. Results? Each of the above substances is composed largely of C, H, and O. What is the dark-colored substance which remains in each case?

Repeat each of the above experiments with the oily fluid prepared in Exp. XXI. Make a record of results. Are its properties identical with the shelf-reagent, H_2SO_4? Is sulphuric acid a efficient drying agent?

(*b*) To 1 cm.^{3} of the fluid prepared in Exp. XXI, add 5 cm.^{3} of water. Test with blue litmus paper. Repeat above, using H_2SO_4. Results?

(*c*) Try the action of the "acid" on a piece of zinc in a test tube. What gas is evolved? Repeat with H_2SO_4. Compare results.

(*d*) Add $BaCl_2$ to a portion of the acid prepared in above experiment. Is the precipitate soluble in HCl?

Does H_2SO_4 yield similar results? Drawing your inference from the results of the above experiments, identify the liquid prepared in Exp. XXI. Write the structural formula for H_2SO_4.

Experiment XXIII.—Hydration of Sulphuric Acid.

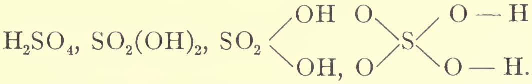
(*a*) Into 5 cm.^{3} of water in a test tube add 10 cm.^{3} of strong H_2SO_4. Is there a change in the temperature of the liquids? What is the probable explanation of the thermal phenomenon?

$$H_2SO_4 + 2H_2O \rightarrow H_2SO_4\text{, Aq} + 17{,}850 \text{ cal.}$$

Is the solution more or less stable than the pure acid? Why?

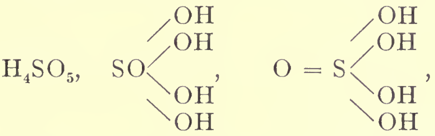
(*b*) Optional. The following interesting experiment is suggested by Freer: Add 9.8 grams of concentrated H_2SO_4 to 1.8 grams of water; place the liquid in a small flask and surround the latter with a freezing mixture of ice and salt; crystals of $H_2SO_4.H_2O$ (H_4SO_5) will form; warm the crystals until they are melted (80° C.), then add 1.8 grams of water; again place in the freezing mixture and crystals of $H_2SO_4.2H_2O$ (H_6SO_6) will separate. Further addition of water is not accompanied by increase of temperature.

H_2SO_4, Normal Sulphuric Acid.



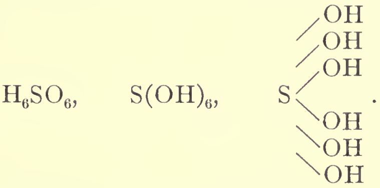
$$H_2SO_4,\ SO_2(OH)_2,\ SO_2{<}\begin{matrix}OH\\OH,\end{matrix}\ \begin{matrix}O\\O\end{matrix}{>}S{<}\begin{matrix}O-H\\O-H.\end{matrix}$$

$H_2SO_4.H_2O$, Tetra hydroxyl Sulphuric Acid.



$$H_4SO_5,\quad SO{<}\begin{matrix}OH\\OH\\ \\OH\\OH\end{matrix},\quad O=S{<}\begin{matrix}OH\\OH\\ \\OH\\OH\end{matrix},$$

$H_2SO_4.2H_2O$, Hexahydroxyl Sulphuric Acid.



$$H_6SO_6,\quad S(OH)_6,\quad S{<}\begin{matrix}OH\\OH\\OH\\ \\OH\\OH\\OH\end{matrix}.$$

Experiment XXIV.—Dissociation of Sulphuric Acid.

Pour 4 cm.³ of concentrated H_2SO_4 into a clean dry test tube; clamp the tube to the ring stand; suspend a 200°–300° C. thermometer so that the bulb will be immersed in the acid; heat the test tube gently with a small flame. Take the reading on the thermometer at the first appearance of the heavy, dense white fumes of SO_3. *Caution.*—Hot H_2SO_4 produces severe burns. Note the thermometer reading frequently, that the thread of mercury may not be allowed to approach too near the top of the tube. Write the equation indicating the dissociation of H_2SO_4. What is the difference between dissociation and decomposition?

Experiment XXV.—Reduction of Sulphuric Acid.

Recall Exp. XI. (*c*), (*d*). Equations?

Experiment XXVI.—Soluble and Insoluble Sulphates.

Test the action of a solution of Na_2SO_4 or dilute H_2SO_4 upon separate solutions of each of the following substances: $AgNO_3$, NaCl, $CaCl_2$,

$Pb(NO_3)_2$, $Cu(NO_3)_2$, KNO_3, $BaCl_2$, $Sr(NO_3)_2$, NH_4Cl, $FeCl_3$. Write the ionic equations for each reaction. Underscore the formula representing the precipitate in each case.

Experiment XXVII.—Optional. Decomposition of Isoluble Sulphates.

Insoluble sulphates, e.g., $BaSO_4$, may be decomposed by fusion with Na_2CO_3; Na_2SO_4, which is soluble in water, being formed. The fused mass is extracted with water and the solution made slightly acid with HCl, after which $BaCl_2$ is added. The substances are usually fused in a crucible.

Note.—The above method is quite generally used for converting insoluble salts into corresponding salts of the alkali metals. Practically all of the salts of sodium and potassium are soluble in water, hence the use of Na_2CO_3 or K_2CO_3 as a flux.

Most sulphates are soluble in water. Silver, calcium, strontium, lead and barium are but slightly soluble in water. Their solubility decreases in the order named.

Experiment XXVIII.—Optional. Reduction of Sulphates and Sulphites.

(*a*) Mix a small quantity of a sulphate or a sulphite with two or three times its weight of pure anhydrous Na_2CO_3; place a portion of the mixture in a depression in a piece of charcoal; using a blow-pipe, direct the reducing flame upon the mixture. Place the fluid mass upon a silver coin or a piece of filter paper moistened with lead acetate; allow a drop of dilute HCl to fall upon the mass. Explain the formation of a black stain. Equations?

Experiment XXIX.—Optional. Sulphur Trioxide. The Manufacture of Sulphuric Acid by the "Contact Process."

(*a*) Put 15 $cm.^3$ of fuming sulphuric acid (disulphuric or pyrosulphuric acid, $H_2S_2O_7$) in a small dry retort provided with a glass stopper and connected with a dry receiver immersed in water. Keep the receiver cool. Heat the flask gently, and observe evolution of the heavy SO_3 fumes which condense to a solid in the receiver. Remove some of the solid by means of a glass rod and put it in a little water. Is heat evolved? Place other portions on pieces of paper and wood. Results?

(*b*) Sulphur dioxide and oxygen do not combine rapidly under ordinary conditions to form sulphur trioxide. At higher temperatures the reaction proceeds relatively slowly. Above 400° C., SO_3 is decomposed into SO_2 and O. It has been found that if the two gases are passed simultaneously over heated finely-divided platinum they combine to form SO_3 which combines readily with water to form H_2SO_4. The above is a general statement of the principles involved in the manufacture of H_2SO_4 by the "contact process."

Prepare platinized asbestos as previously directed; place it in a long hard glass tube. Devise a method for passing oxygen and sulphur dioxide through the tube. The gases should be dry. Collect the gases in a dry receiving flask. Is there any evidence of SO_3 being formed? Now gently heat the tube beneath the asbestos. Results? When the products are added to water, the solution may be tested for sulphuric acid.

$$\begin{aligned} &SO_2 + O \rightarrow SO_3 + 32{,}100 \text{ cal.} \\ &S + O_3 \rightarrow SO_3 \text{ (liquid)} + 103{,}200 \text{ cal.} \\ &SO_3 + H_2O \rightarrow H_2SO_4 + 21{,}300 \text{ cal.} \\ &(H_2SO_4, Aq) = 17{,}800 \text{ cal.} \\ &(S, O_3, Aq) = \ ? \text{ cal.} \\ &(H_2, S, O_4) = \ ? \text{ cal.} \end{aligned}$$

Experiment XXX.—Preparation of a Soluble Thiosulphate.

Dissolve 5 grams of sodium sulphite, $NaSO_3$ in 20 cm.^{3} of H_2O, then add 3 grams of finely divided sulphur, e.g., flowers of sulphur. Boil the mixture for 10 or 15 minutes. Replace the water which has evaporated; filter. Pour the filtrate into a small beaker or a crystallizing dish. Sodium thiosulphate, $Na_2S_2O_3.5H_2O$, commonly called hyposulphite of soda ("hypo"), will crystallize out of the solution. Acids, e.g., H_2SO_4, decompose thiosulphates with the formation of a sulphate, sulphurous acid and the liberation of free sulphur. Try the action of acids upon the crystals. Results? Equations?

Experiment XXXI.—Preparation of an Insoluble Thiosulphate. Decomposition of Thiosulphates by Heat.

(*a*) To a few cm.^{3} of a solution of a soluble thiosulphate add a few drops of a $AgNO_3$ solution. Observe the color of the precipitate. Heat the mixture and note the formation of black-silver sulphide. Is SO_2 evolved? Is free sulphur liberated? Equations?

(*b*) Lead acetate may be substituted for $AgNO_3$ and (*a*) repeated.

Experiment XXXII.—Oxidation of Sodium Thiosulphate to a Tetrathionate by the Action of Iodine.

Prepare a solution of sodium thiosulphate; add a little starch water. Dissolve a small quantity of iodine in a potassium iodide solution. To 5 cm.^{3} of the thiosulphate solution add the solution of iodine drop by drop until the solution turns blue. Explain. Equations?

Note.—The titration of iodine against sodium thiosulphate with starch as an indicator is a process frequently used in analytical chemistry.

Experiment XXXIII.—(Quant.) Compare the electrical conductivities of pure concentrated H_2SO_4 and a 5N solution of same acid. Explain results. The *activity* of an acid depends on what? Would you infer that H_2SO_4 in aqueous solution is *active* as an acid? Are the electrical conductivities of acids related in any way to their *activities?* Explain. Write the ionic equation indicating the different particles present in an aqueous solution of sulphuric acid.

Experiment XXXIV.—(Quant.) Specific Gravity of Sulphuric Acid.

Devise a method for determining the specific gravity of sulphuric acid. What is the sp. gr. of the concentrated H_2SO_4 which is found among the shelf-reagents?

Experiment XXXV.—(Quant.) Contraction in Volume When Sulphuric Acid and Water are Mixed.

By means of a pipette place 10–20 cm.³ of concentrated H_2SO_4 in a long narrow test tube or a colorimetric tube; carefully add one-half its volume of water; mark the volume occupied by the two liquids. Now mix the two liquids by careful manipulation of the tube. Note the change in temperature of the liquids. Cool the mixture and determine the amount of contraction. Does the acid undergo hydration?

Although several factors may contribute to the contraction, it is known that "water of hydration" occupies less space than ordinary water.

OXACIDS OF SULPHUR.

H_2SO_3	Sulphurous acid.
H_2SO_4	Sulphuric acid.
$H_2S_2O_3$	Thiosulphuric acid.
$H_2S_2O_4$	Hyposulphurous acid.
$H_2S_2O_5$	Pyrosulphurous acid.
$H_2S_2O_6$	Dithionic acid.
$H_2S_2O_7$	Pyrosulphuric acid.
$H_2S_2O_8$	Persulphuric acid.
$H_2S_3O_6$	Trithonic acid.
$H_2S_4O_6$	Tetrathionic acid.
$H_2S_5O_6$	Pentathionic acid.
$H_2S_6O_6$	Hexathionic acid.

SELENIUM, Se.

At. Wt. 79.2 Mol. Wt. 158.4.
See Text-book and Lecture Notes.

TELLURIUM, Te.

At. Wt. 127.6. Mol. Wt. (?).
See Text-book and Lecture Notes.

The following table gives a general view of the similarity of the elements of this group:

Physical Properties	Oxygen	Sulphur	Selenium	Tellurium
Atomic weight	16.0	32.06	79.2	127.6
State or phase	Gas	Solid	Solid	Solid
Color	Colorless,	Pale-Yellow	Grayish-White	Silver-White
Specific gravity	1.13 (at—182°)	2.02 (Rhombic)	4.5 (Crystalline)	6.3?
Specific heat	<——————————————<			
Melting-point	Below —223°	111.5°	217°	452°
Boiling-point	—182°	445°	675°	1400°
Chemical Properties				
Heat of formation of H- derivatives	H_2O 57,000 cal.	H_2S 2,730 cal.	H_2Se —5,400 cal.	H_2Te —19,400 cal.
Stability of H-derivatives	<——————————————<			
Heat of formation of O- derivatives	O_2,O(gas) 32,400 cal.	SO_2(gas) 71,000 cal.	SeO_2(solid) 57,700 cal.	TeO_2(solid) 77,000 cal.
Oxacids	. . . .	H_2SO_3 ? H_2SO_4 (liquid)	$H_2S_3O_3$ (solid) H_2SeO_4 (liquid)	H_2TeO_3 (solid) H_2TeO_4 (liquid)
Heat of formation of Cl-derivatives	O,Cl_2 —18,000 cal.	S_2Cl_2 14,300 cal.	Se_2Cl_2 22,200 cal.	$TeCl_4$ 77,400 cal.
Metallic Properties (Physical)	>——————————————>			

PROBLEMS.

1. How many grams of sulphur in 1l. of H_2SO_4, sp. gr. 1.84? How many grams of oxygen? Of hydrogen?

2. How many grams of H_2SO_4 will be required to neutralize 10 grams of $Ba(OH)_2$?

3. How many cm.^{3} of a 5N solution of H_2SO_4 will be required to neutralize 50 cm.^{3} of 1N of NaOH?

4. Calculate the heat of formation of anhydrous sulphuric acid from its elements, i.e., $(S, O_4, H_2) = ?$ Ans. 192,900 cal.

5. What is the heat of formation of sulphuric acid from its elements in dilute aqueous solution, i.e. $(H_2, S, O_4, Aq) = ?$ Ans. 210,700 cal.

CHAPTER XVIII.

NITROGEN AND THE ATMOSPHERE.—THE HELIUM FAMILY.

NITROGEN, N.

At. Wt. 14.01. Mol. Wt. 28.02.

Nitrogen is a colorless, odorless and tasteless gas. At ordinary temperatures it is chemically inert.

Preparation and Properties of Nitrogen.

Experiment I.—Preparation of Nitrogen.

(*a*) Assemble the parts of the oxygen or hydrogen generator. Place about 5 grams of sodium or potassium nitrite, $NaNO_2$, KNO_2, and 2 grams of ammonium chloride, NH_4Cl, in the generating test tube or flask; add 10–15 cm.^{3} of water; insert stopper provided with delivery tube; clamp the tube to ring-stand; heat gently by waving the flame under the tube. Be careful not to overheat the mixture. Fill three bottles with the gas by displacement of water. Proceed with Exp. II.

$$(1)\quad NaNO_2 + NH_4Cl \rightarrow NH_4NO_2 + NaCl$$
$$(2)\quad NH_4NO_2 \rightarrow \overline{N_2} + 2H_2O.$$

(*b*) Alternative method. The gas may be prepared by heating ammonium nitrite, NH_4NO_2, which decomposes into water and nitrogen.

Experiment II.—Properties of Nitrogen.

Has the gas color, odor, taste? Is it inflammable? Will it support combustion? Does it unite readily with other elements? Prove its inertness in this respect. Is the gas heavier or lighter than air?

Experiment III.—(Quant.) Determination of the Weight of a Liter of Nitrogen.

Provide a round-bottomed 250 cm.^{3} flask (Fig. 31) with a rubber cork through which passes a piece of glass tubing about 8 cm. in length; attach a piece of rubber tubing about 5 or 6 cm. long to the outer end of the glass tube and wire it firmly. Pour about 30 cm.^{3} of water into the flask, then firmly press the stopper into place; make a mark on the neck of the flask at the bottom of the stopper so as to be able to determine the exact contents of the flask when the stopper is in place. Boil the water with a small flame until all the air has been expelled from the flask. Allow the steam to escape for 5 or 6 min., then close the rubber tube with a strong clip, and quickly remove the flame. Attach a fine wire to the neck of the flask by which it may be suspended during the process of weighing. When the flask has cooled to the temperature of the laboratory, wipe and carefully weigh it. Read the temperature and barometric pressure in the balance-room. Place a beaker of water so that the rubber *siphon tube* of an aspirator bottle (Fig. 32) partially filled with nitrogen is made to dip beneath the surface of the water. Connect the flask with the *delivery tube* of the aspirator; the clip is gradually opened allowing a slow stream of nitrogen to enter the flask. Now raise the beaker of water so that the water in it will be at a higher level than that in the aspirator. Close the clip, disconnect from the aspirator delivery tube. Open the clip for an instant to establish atmospheric pressure in the flask, then weigh again. The increase in weight represents the weight of the nitrogen. From the table in the appendix ascertain the aqueous tension at the observed temperature; subtract this from the barometric pressure. Determine the volume of the flask by filling with water to the mark placed on the neck and weighing it. Calculate the weight of a liter of nitrogen at 0° C. and 760 mm. What is the ratio of the weights of equal volumes of hydrogen and nitrogen? What is the weight of the molar volume of the gas?

FIG. 31.

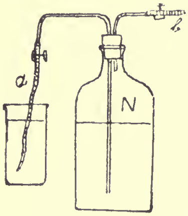


FIG. 32.

THE ATMOSPHERE.

The *atmosphere, or air* as it is usually termed, is the gaseous envelope surrounding the earth. It is a mixture, the components of which may be divided into two classes: (a) those components, oxygen, nitrogen, argon and other members of the helium group, which are practically constant in amount; (b) components which are variable in amount, e.g., carbon dioxide, water vapor, ozone, dust, traces of ammonia, minute quantities of solids like ammonium nitrate and ammonium carbonate, organic matter, etc.

The comparatively recent discovery of five gaseous elements in the air has given a new impetus to the investigation of the composition of the atmosphere. It is rather remarkable that these five elements constitute a natural group, known as the *helium group.* The student is referred to the well-known work by Sir William Ramsay, "The Gases of the Atmosphere."

Components of the Atmosphere.

Experiment IV.—(Quant.) Determination of the Amount of Oxygen in the Air. Nitrogen.

(*a*) Absorption or Pyrogallate Method. See Exp. X. "Oxygen." Repeat experiment. Calculate the percentage of oxygen by volume in the air. Test the residual gas as to odor, taste, inflammability. What is the color of the gas? Will it support combustion? Are its properties similar to those of nitrogen? If this residual gas were pure nitrogen instead of nitrogen mixed with traces of other gases, what would be the percentage of nitrogen in the air?

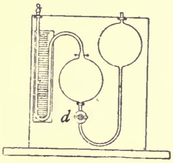


Fig. 33.
(*Smith and Keller.*)

Note.—Hempel's burette and compound pipette as apparata in which to measure and absorb the gas may be used instead of that suggested above. See Hempel's "Gas Analysis," translated by L. M. Dennis.

(*b*) Explosion method. Substitute Hempel's explosion pipette (Fig. 33) for the absorption pipette used in (*a*), and proceed as follows: To 25 cm.^{3} of air contained in the burette add 25 cm.^{3} of pure hydrogen, then pass the mixture into the explosion pipette; close the pipette. (Instructions.) Pass an electric spark through the mixture. Return the residual gas to the burette and measure. What is the composition of this gas? How much of the contraction was due to oxygen? Calculate the percentage of oxygen in the air.

Experiment V.—Removal of Oxygen from the Air. Determination of the Approximate Percentage of Nitrogen in the Air.

(*a*) Place a small piece of yellow phosphorus either in an evaporating dish floating on the water or in a small crucible resting in a depression in a large cork which floats on the water in the pneumatic trough. Ignite the phosphorus and quickly place a bell-jar or an inverted beaker over the crucible (Fig. 34). Keep the rim below the surface of the water that no gas may escape. Hold the bell-jar in this position until the dense heavy

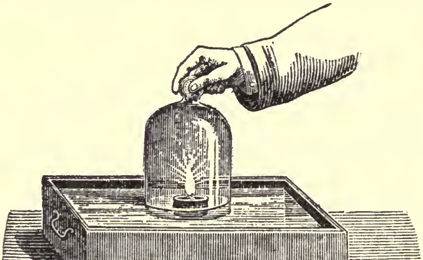


Fig. 34.

fumes of phosphorus pentoxide, P_2O_5, disappear. Note that the water has risen in the jar. Lower the bell-jar until the water on the inside and outside have the same level; mark this level on the jar. Place a glass plate over the mouth of the bell-jar and quickly invert it; test the gas with a burning match. Results? Test the water in the trough with blue litmus paper. Explain. How many cm.³ of water are required to fill the jar to the mark placed in it? How many cm.³ are required to fill it? Calculate the percentage of nitrogen in the air. Of Oxygen. Equations?

(*b*) If a piece of yellow phosphorus is inserted into a measured volume of air contained in a graduated tube (Fig. 35) over water or mercury, the phosphorus will combine slowly with the air forming P_2O_5 which unites with water to form phosphoric acid. The phosphorus should be allowed to remain in contact with the enclosed air for 24 to 48 hours. The water will slowly rise in tube to take the place of oxygen. In determining the volume of the residual gas the usual corrections should be applied. The gas may be tested for nitrogen.

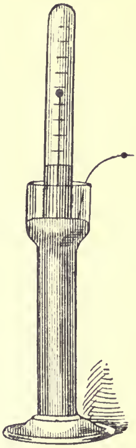


FIG. 35.

Experiment VI.—Preparation of "Atmospheric Nitrogen."

Fit each end of a piece of hard glass tubing 25–30 cm. long, with a cork through which passes a short piece of glass tubing; clamp the tube in a horizontal position; place a large plug of copper turnings in the middle of the tube; connect tube in series with wash bottles, No. 1 and No. 2, containing respectively a strong solution of KOH and concentrated H_2SO_4; the latter wash bottle is connected with an aspirating bottle filled with mercury or water. Heat the copper red-hot; open the stop cock on the siphon of the aspirator and allow the liquid to be siphoned off drop by drop or in a slow stream. When the system has been swept free of air, quickly substitute another aspirator which has been previously filled. When three-fourths of the liquid has run out, close stop cock on siphon and disconnect the aspirator from the wash bottle and attach a delivery tube; raise the end of the siphon and attach a small funnel; pour water into the funnel; open stop cock on siphon; the water will drive the gas out through the delivery tube. Collect several bottles of the gas by displacement of water, and apply the usual tests for nitrogen. Examine the copper. Explain change of color.

Experiment VII.—Presence of Water Vapor in the Atmosphere.

(*a*) Place small quantities of calcium chloride, $CaCl_2$, and phosphorus pentoxide, P_2O_5, on separate watch-glasses and expose them to the air. Examine them after 10 or 15 min. Results? Conclusions? Touch the moist P_2O_5 with a piece of blue litmus paper. Results? Explain. Equation?

Which of the two substances apparently absorbs moisture the more rapidly? Name another familiar substance which will remove moisture from the air.

(*b*) A quantitative determination of the amount of moisture in the air may be made by drawing a given volume of air through a U-tube filled with glass beads and P_2O_5 by means of an aspirator. The increase in weight of the P_2O_5 will represent the amount of moisture absorbed from a known volume of air. (Instructions.) Substances which absorb moisture are said to be *hygroscopic.*

Experiment VIII.—Presence of Carbon Dioxide in the Atmosphere.

(*a*) Place 5 cm.^{3} of a clear solution of calcium hydroxide, $Ca(OH)_2$, or barium hydroxide, $Ba(OH)_2$, in a test tube. By use of a glass tube force air (carbon dioxide) from the lungs through the solution until the latter has a milk-like appearance, due to the formation of calcium carbonate, $CaCO_3$. Equation?

Half fill another test tube or a wash bottle with a $Ca(OH)_2$ solution (lime-water) and draw air through the clear solution for several minutes by means of a filter pump or an aspirator. (If all the apparatus is not available expose the solution to the air.) Results? Conclusions as to the presence of CO_2 in the air?

(*b*) Repeat the above experiment, but pass the air through a strong solution of NaOH or KOH before it is allowed to enter the $Ca(OH)_2$ solution. Results? Explain.

(*c*) The student is referred to works on "gas analysis" for methods of making a quantitative determination of the CO_2 in the air. Report one method.

Experiment IX.—Absorption of Oxygen and Nitrogen by Magnesium and Calcium. Argon, etc.

Prepare a mixture composed of equal parts of magnesium powder and freshly-ignited calcium oxide. Keep the mixture perfectly dry. Introduce a few grams of this mixture into a piece of combustion tubing sealed at one end and about 20 cm. in length; clamp the tube in a horizontal position; connect the open end of the tube with a delivery tube of smaller bore and about 80 cm. long. The delivery tube should be bent so that its free end may be immersed in a vessel of mercury 76 cm. below the combustion tubing. Heat the mixture gently, then gradually increase the temperature to that of a powerful burner. Continue to heat the tube until the mercury no longer rises in the vertical tube. What is the residual gas? What is the probable composition of the solid matter in the tube?

Experiment X.—Table of the Composition of the Air.

Prepare a tabulated statement of the average composition of the atmosphere. Before attempting to prepare the table, consult various reference works. Give the names and authors of the books consulted.

Experiment XI.—(Quant.) Determination of the Weight of a Liter of Air. The weight of a liter of air may be determined by a method similar to that described under "Nitrogen."

THE HELIUM FAMILY.

The members of this natural group exhibit many close resemblances, e.g., remarkable inertness, monatomic nature of their molecules, etc. They also manifest that gradation of properties which has been observed in the other natural groups of elements, e.g., atomic volumes, densities, refractive indices, etc. At first there seemed to be no place within the periodic system for these elements, but it has been pointed out that they may not unnaturally occupy the positions of transition elements between the highly negative elements, the halogens, and the strongly positive elements, the alkali metals. With the exception of argon whose atomic weight appears to be too large, the atomic weights of the elements naturally place them in this position.

	Symbol	Density	Atomic weight	Absolute critical temp.	Critical pressure (mm.)
Helium (sun)	He	2.0	4.0	....	....
Neon (the new one)	Ne	10.0	20.0	....	....
Argon (the lazy one)	A	19.9	39.9	155.6°	40,200
Krypton (the hidden one)	Kr	40.9	81.8	210.5°	41,240
Xenon (the stranger)	Xe	64.0	128.0	287.8°	43,500

"Critical data" from Travers, Experimental Study of Gases.

Ramsay gives the following table as representing an estimate of the quantities in which the individual gases of the helium family are present in the atmosphere. The data was obtained by distillation of "atmosphere" air, or argon.

Helium	1 to 2 parts per 1,000,000 of air.
Neon	1 to 2 parts per 100,000 of air.
Argon	0.937 part per 100 of air.
Krypton	1 part per 1,000,000 of air.
Xenon	1 part per 20,000,000 of air.

Expressed in parts per 1000:

Argon	9.37
Neon	0.01
Helium	0.001
Krupton	0.001
Xenon	0.00005

It is highly probable that the helium quickly passes out from our atmosphere into space, as a gas of so low a density must have, according to the "kinetic theory" of gases, a velocity greater than the "critical velocity" at the earth's surface which has a calculated value of 6.9 miles per second. "The quantity of helium," says Travers, "which is constantly being given off by mineral springs is, however, enormous, so that it is probable that the amount present in the atmosphere does not tend to diminish."

The student is earnestly requested to examine the following books in connection with the work of this chapter.

Experimental Study of Gases.—Travers. Gas Analysis—Hempel Dennis. Liquefaction of Gases.—Hardin. The Gases of the Atmosphere.—Ramsay.

PROBLEMS.

1. Dumas, in determining the composition of air by passing it over heated copper and measuring the residual nitrogen, tabulated the following data:

Weight of tube and copper before experiment.......	120.00 grams.
Weight of tube and copper after experiment.........	121.15 grams.
Weight of globe exhausted........................	852.00 grams.
Weight of globe and nitrogen......................	855.85 grams.

Calculate the percentage of nitrogen and oxygen by weight. By volume.

2. Calculate the weight of 5 l. of air. Of 4.2 l. Of 9 l.

3. A mixture of 25 cm.^{3} of air and 50 cm.^{3} of hydrogen was exploded, and the residue measured 60.3 cm.^{3} What was the percentage of oxygen in sample of air?

4. A student introduced 50.6 cm.^{3} of air into a Hempel absorption pipette containing alkaline pyrogallol. After agitating the pipette for 20 min. the gas was returned to the Hempel burette, and found to occupy 40.03 cm.^{3} when measured under original conditions. Which component of the atmosphere was removed? Calculate the percentage of this component by volume.

5. Dumas and Boussingault in 1841 found 12.373 grams of nitrogen and 3.68 grams of oxygen in a sample of air. What per cent. of each component did they find?

6. A U-tube containing phosphorus pentoxide was found to weigh 30.6293 grams. A volume of air which weighed 30.4268 grams was passed through, after which the weight of the tube was found to be 31.0517 grams. Calculate the percentage of moisture present in the air.

7. It has been found that when air dissolves in water, the ratio of oxygen to nitrogen in the dissolved air is no longer 1:3.71 (approx.) but 1:? The absorption coefficients of oxygen and nitrogen for water as given by Bunsen are, O = .0411 and N = .0203, at 760 mm. Calculate the ratio of free oxygen to nitrogen in the water when the total atmospheric pressure is 760 mm. *Hint.*—Recall Henry's Law and Dalton's Law of Partial Pressures.

8.—What properties manifested by the atmosphere led men to believe that it was a chemical compound?

Enumerate the reasons which lead us to regard the air as a mixture.

CHAPTER XIX.

NITROGEN FAMILY.

Nitrogen	N,	14.01
Phosphorus	P,	31.0
Arsenic	As,	75.0
Antimony	Sb,	120.2
Bismuth	Bi,	208.0

These five elements are grouped together not only because of their atomic weight relationships, but in virtue of a similarity in chemical properties. Antimony and bismuth, especially the latter, possess decidedly metallic characteristics. With the exception of bismuth, they form poisonous gaseous derivatives with three atoms of hydrogen. The chief oxygen compounds of each are of R_2O_3 and R_2O_5 types. They form generally unstable derivatives by combining with three atoms of a halogen. These halogen compounds are particularly unstable in the presence of water. It should be noted that with increase of atomic weight, the properties of the oxides of these elements vary gradually from strong acid anhydrides to weak basic oxides.

NITROGEN, N.

At. Wt. 14.01 Mol. Wt. 28 02.

Preparation and Properties of Nitrogen.

Experiment I.—Recall Exps. I and II. "Nitrogen and the Atmosphere."

Hydrogen derivatives, NH_3, $(NH_2)_2$, N_3H.

Experiment II.—Preparation and Properties of Ammonia Gas and Ammonium Hydroxide.

(*a*) Preliminary Experiment. Dissolve about 1 gram of ammonium chloride, NH_4Cl, in a few cm.^{3} of water. Boil the solution. Do you detect the odor of ammonia? Test the escaping vapors with moistened pieces of red litmus paper and turmeric paper. Results? Add a few drops of a NaOH solution. Repeat previous tests. Results? Hold a glass rod which has been moistened with strong HCl just above the mouth of the test tube. Results? What is the name of the substance formed by the interaction of the ammonia gas and HCl? Equations? Repeat, using KOH instead of NaOH. Other salts of ammonia may be substituted for NH_4Cl.

(*b*) Laboratory method for preparation of ammonia gas. Support a small flask by use of wire gauze on a ring-stand; fit a stopper provided with a right-angled delivery tube to the flask; to the delivery tube connect by means of rubber tubing a right-angled tube which is turned *upward* that the gas may be collected by upward displacement of the air.

Mix together in a mortar about 20 grams of calcium oxide, CaO (quicklime), or calcium hydroxide, $Ca(OH)_2$, and 10 grms of NH_4Cl. Odor? Place the mixture in the flask and heat very gently; lay a piece of cardboard with a hole in it over the mouth of a dry bottle; invert the bottle over the delivery tube. When the bottle is filled with gas, test by waving air from the bottle to the nose or by placing a piece of red litmus paper moistened with water in the mouth of the bottle; cover it and place it with mouth down upon the desk. Collect four bottles of the gas. Turn the mouth of the delivery tube down, allowing it to barely touch the surface of 10 cm.^{3} of water in a test tube. Is there any evidence that the gas is dissolving in the water? Raise the test tube cautiously until the mouth of the delivery tube is about 2 cm. below the surface of the water? Do bubbles of ammonia gas escape from the water? Explain. Do you notice any change in the temperature of the water in the test tube?

Lower the tube to its original position and continue to heat flask for a few minutes, then remove the aqueous solution of the gas and extinguish the flame. Raise the flask from the gauze and place it on a piece of dry cloth and allow it to cool. Explain the purpose of this last operation. When the flask cools, observe if there is any evidence of water in the generating flask. Explain. Equations?

(*c*) Properties. In view of the method used in collecting the gas, what are your conclusions as to the density of ammonia gas as compared with that of the air? Test the inflammability of the gas. Results? Will the gas support combustion? (The gas will burn in an atmosphere of pure oxygen. Pass a stream of pure oxygen through concentrated solution of ammonia gas heated in a 50 cm.^{3} flask. Apply a light to the mouth of the flask. Explain. Equations?) Test the gas with moist turmeric paper and with litmus paper. Results? Moisten a glass rod with concentrated HNO_3; insert it into a bottle of the gas. Results? Equations?

(*d*) Solubility of the gas. Ammonium hydroxide. Place a bottle of the gas mouth downward in a vessel of water. Hold it in this position for 4 or 5 minutes. Results. Explain. Examine the solution of ammonia prepared in (b). Test it with litmus paper. Hold a rod dipped in concentrated HCl over the solution. Results? What name is applied to this aqueous solution of ammonia? Indicate its formation by use of an equation.

(*e*) Stability of ammonium hydroxide. Put 5 cm.^{3} of NH_4OH in an evaporating dish and boil it gently for a few minutes. Note the escape of the ammonia gas. Place 5 cm.^{3} of NH_4OH in a small beaker and allow it to stand exposed to the atmosphere for 24 to 48 hours. Is the odor as strong as before? What do you infer as to the stability of NH_4OH?

(*f*) Does NH_4OH manifest the properties of a base or an acid? Contrast it with the aqueous solutions of hydrogen compounds of sulphur. Are the basic properties of NH_4OH due to the ammonia gas or the hydroxyl group formed by its combination with water? Recall the electrical conductivity of NH_4OH. Is NH_4OH a strong base? State the reasons for your answer. What specific name do we apply to NH_4? Why? Write the structural formulæ for NH_3 and NH_4OH.

$$N + H_3 \rightarrow NH_3 + 11{,}900 \text{ cal.}$$
$$NH_3 + Aq \rightarrow NH_3,Aq + 8500 \text{ cal.}$$

Ice will melt in gaseous ammonia. Explain.

Experiment III.—Production of Ammonia by Destructive Distillation of Nitrogenous Substances.

Heat separately in a test tube small quantities of each of the following: hair, wool, bone, gelatin, feathers. Observe the effect of heat upon these substances. Test the action of the fumes which are evolved upon turmeric paper or red litmus paper. Results? Define destructive distillation?

Experiment IV.—Preparation of Ammonium Salts.

(*a*) Preparation of ammonium chloride. Place 5 $cm.^3$ of NH_4OH (shelf-reagent) in a beaker; neutralize the base with dilute HCl, using litmus paper or phenolphthalein as an indicator; evaporate the solution until crystals begin to form on the sides of the vessel, then pour the solution into a crystallizing dish and observe the formation of crystals as the solution cools. Write the formula for the substances formed.

(*b*) Preparation of ammonium sulphate. Proceed as in (*a*), substituting dilute H_2SO_4 for HCl. Are these salts soluble in water? Are they conductors of electricity? If so, indicate by equations the nature of the electrolytic dissociation.

Experiment V.—Decomposition of Ammonium Salts. Dissociation.

(*a*) Place a small quantity of NH_4Cl in a piece of hard glass tubing open at both ends. Clamp the tube in a slightly inclined position; heat the tube strongly and hold moist pieces of each kind of litmus paper in each end of the tube. Results? Explain. Recall Exp. III. "Chemical Equilibrium."

(*b*) Repeat (*a*), using $(NH_4)_2SO_4$ instead of NH_4Cl.

Nitrogen and the Halogens.

Experiment VI.—Preparation of an Endothermic Compound. Nitrogen Tri-iodide.

To a small quantity of powdered iodine in an evaporating dish, add a little strong NH_4OH. Frequent stirring will assist the digesting of the iodine by the NH_4OH. Let the mixture stand for half an hour. Filter.

Place the black sediment upon several filter papers. Spread the wet papers at a distance from one another and allow them to dry. The dry black powder contains impure NI_3, which is extremely explosive. When touched with a feather it readily explodes. The shock produced by the tread of a fly, or falling dust particles sometimes cause it to explode. The student should prepare only very small quantities of the substance.

(1) $2NH_4OH + I_2 \rightarrow NH_4IO + NH_4I + H_2O.$
(2) $3NH_4IO \rightarrow N_2H_3I_3 + KOH.$
(3) $N_2H_3I_3 \rightarrow NH_3 + NI_3.$
$(N,Cl_3) = -38,100$ cal.
$(N,I_3) = -$ (? cal.).

Experiment VII.—(Quant.) Determination of the Weight of a Liter of Ammonia Gas.

Fill a 250 $cm.^3$ flask with the gas by *upward* displacement of air. Both flask and gas must be perfectly dry; the gas may be dried by passing it through two tubes filled respectively with small pieces of lime and soda-lime. A loose plug of cotton should be placed in the neck of the flask to prevent diffusion. When the flask is filled, slowly withdraw the tube and cork at once. Wipe the flask and place it in the balance-room. Read the thermometer and the barometer. Weigh the flask. Determine the volume of the flask. Calculate the weight of this volume of air, if 1 $cm.^3$ of air at 0° C. and 760 mm. weighs .001293 gram subtract this weight from the weight of the flask when filled with air. The remainder is the weight of the vacuous flask. What is the weight of one liter of the gas at 0° C., 760 mm.? Of the molar volume? How many times heavier is one liter of ammonia gas than a liter of hydrogen? What is the ratio of their molecular weights?

Experiment VIII.—(Qual.). Determination of the Composition of Ammonia Gas.

Instructions.—Perfectly dry ammonia gas is passed very slowly over heated magnesium powder placed in a piece of combustion tubing. Loose plugs of cotton are placed in the end of the drying tubes containing, respectively, quicklime and soda-lime. The gaseous product is collected over dilute H_2SO_4 placed in a small glass dish. The greenish powder which is formed in the combustion tubing is tested by pouring a portion of it into a test tube half filled with water. Test the gas which is liberated. Is it ammonia? Equation?

It is suggested that the ammonia gas be prepared by heating concentrated NH_4OH over a low flame in a generating flask provided with a thistle tube. The flask should rest upon a sand bath or a sheet of asbestos.

Caution.—Do not heat the thin layer of magnesium powder until the apparatus is flooded with ammonia gas.

Experiment IX.—(Quant.) L.T. Composition of Ammonia Gas. (Volumetric.)

A very desirable form of the apparatus necessary for the performance of this experiment may now be secured from any of the chemical laboratory supply houses. It is usually listed with the "Hofmann Lecture Apparatus." A long glass tube, sealed at the lower end, and provided at the upper end with a glass stop cock, which communicates above with a small funnel-like chamber, which can be stoppered, is filled with chlorine over a saturated solution of sodium chloride. The tube is allowed to stand mouth downward in the solution for sometime in order to let the liquid drain out of it, after which the stop-cock is closed and the tube on removal from the solution is placed in an upright position. The small chamber above the stop cock is now nearly filled with concentrated ammonium hydroxide and the stopper inserted. Slightly open the stop cock and allow the ammonium hydroxide to pass into the lower tube drop by drop. The evolution of considerable heat and usually a faint flash of light, together with the formation of dense white fumes, indicate to the experimenter that chemical reaction is taking place. Great care must be exercised to prevent the escape of any gas or the entrance of any air into the tube when the stop cock is opened. After nearly all of the ammonium hydroxide has been allowed to pass into the tube, fill the funnel as before and permit the liquid to pass gradually into the tube. Close the stop cock. Fill a large beaker and the funnel with dilute sulphuric acid; fit a tube bent twice at right angles into a cork; fill the bent tube with the acid solution and fit the cork to the funnel; place the other end of this bent tube in the beaker of acid. The long tube should now be immersed in a tall cylinder filled with water at the temperature of the laboratory. Open the stop cock and let the acid drain slowly into the lower tube; if the operation has been successful, the acid will flow into the tube until it is two-thirds full. What is the residual gas? Test it with a lighted match. What are your conclusions in regard to the volumetric relations of the two constituents of ammonia gas? Write the equations for the reactions involved in the above experiment.

$$\underset{20,600\text{ cal.}}{NH_3,Aq} + 3Cl \rightarrow \underset{3 \times 39,300\text{ cal.}}{3HCl,Aq} + N + 97,300\text{ cal.}$$

Experiment X.—(Quant.) L.T. Volumetric Composition of Ammonia Gas. Chemical Equilibrium.

(*a*) Collect about 20 cm.^{3} of pure dry ammonia gas in a perfectly dry eudiometer by displacement of mercury. Allow the apparatus to remain undisturbed for 10 or 15 min. The eudiometer should be clamped in a vertical position in the trough of mercury (Fig. 36). Take the reading of the thermometer suspended in the mercury, and record it together with the barometric reading and the height of the mercury in the eudiometer. Reduce the volume of gas to standard conditions.

Connect the platinum wires of the eudiometer with an induction coil and pass sparks through the gas for 30 min., or until the volume of the gas is practically constant. Allow the apparatus to remain undisturbed for 10 or 15 min. then tabulate data as before. Reduce this final volume to standard conditions. State the ratio of the original and final volumes. Explain, indicating the involved reactions by means of equations. (*b*) or (*c*) may be performed at the discretion of the instructor.

(*b*) Continuation of (*a*). The relative volume of hydrogen and nitrogen may be determined by admitting sufficient dry oxygen to combine with all of the hydrogen and exploding the mixture. The remaining volume, of course, is nitrogen, ignoring aqueous tension. It is customary to admit 5–10 cm.³ of oxygen in excess of that required to combine with the hydrogen.

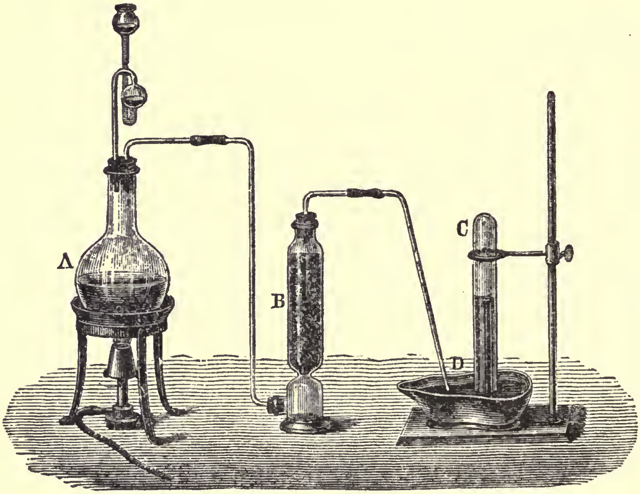


FIG. 36.

(*c*) Chemical equilibrium. Continuation of (*a*). If a little sulphuric acid is admitted above the mercury in the eudiometer and the mixture of gases "sparked," the action will be reversed and the volume of the mixture will gradually decrease until all of the gas disappears. Explain. Interpret the following equations:

$$(2\% - 5\%)\ 2\ NH_3 \rightleftarrows N_2 + 3H_2\ (95\% - 98\%).$$

$$\begin{array}{c} 2\ NH_3 \rightleftarrows N_2 + 3H_2. \\ \downarrow \\ H_2SO_4 \longrightarrow (NH_4)_2SO_4. \end{array}$$

Oxygen Derivatives.

Experiment XI.—Preparation and Properties of the Oxides of Nitrogen.

(*a*) Nitrous oxide (nitrogen monoxide), N_2O. Place about 10 grams of ammonium nitrate, NH_4NO_3, in the large test tube used for generating oxygen; provide the tube with a cork which is fitted with a delivery tube. Heat the test tube gently. Collect three bottles of the gas over warm water by displacement of water. Observe the color and odor of the gas. Is it inflammable? Ascertain if it will support combustion by lowering a glowing splint into a bottle of the gas. Results? What other gas does it resemble in its properties? How can they be distinguished? Explain the action of nitrous oxide, N_2O, in supporting combustion. Equations?

$$(1)\quad (N_2,O) = -17{,}700 \text{ cal.}$$
$$(2)\quad (N_2O,O) = -24{,}800 \text{ cal.}$$

In view of the above experiments and equation, would you conclude that N_2O is stable or unstable? Is it an endothermic or exothermic compound? Indicate the nature of the decomposition of NH_4NO_3 by means of an equation.

Note.—Equation (2) reveals the reason why N_2O is not reactive; i.e., does does not combine with oxygen to form the higher oxides.

(*b*) Nitric oxide (nitrogen dioxide), N_2O_2 and NO. Place about 15 grams of copper turnings in a generating flask provided with a thistle tube and a delivery tube. Add 15 cm.³ of dilute HNO_3, then add strong HNO_3 until there is a brisk evolution of gas. The addition of a little cold water will diminish the speed of the reaction. When the brownish fumes have been swept out of the apparatus, fill four bottles with the gas by water displacement. What is the color of the gas? Lift one of the bottles from the water so as to admit air. What takes place? What is formed? Is the gas inflammable? Will it support combustion? Test by adding a few drops of CS_2 to a bottle filled with NO; shake well, then bring a flame near the mouth of the vessel. Results? Explain. Would you infer that NO is stable or unstable? Pass the gas into warm concentrated HNO_3. Notice the formation of N_2O_3 and N_2O_4 which impart a brown, green or blue color to the solution. Equation? Repeat, using a dilute solution of potassium permanganate, $KMnO_4$, acidified with dilute H_2SO_4. Results? Equations? Does the gas act as an oxidizing or a reducing agent? Pass a current of NO into a strong solution of ferrous sulphate, $FeSO_4$. Results? Equation?

$$(1)\quad (N,O) = -21{,}500 \text{ cal.}$$
$$(2)\quad (N_2,O_4) = -2{,}700 \text{ cal.}$$
$$(3)\quad (2NO,O_2) = 40{,}500 \text{ cal.}$$
$$(4)\quad (NO,O) = 13{,}450 \text{ cal.}$$
$$(5)\quad (2NO_2,O) = 2{,}800 \text{ cal.}$$

After inspecting the above equations, what are your conclusions as regards the readiness with which NO combines with oxygen, and conversely, the ability of these higher oxides to oxidize?

(*c*) Nitrogen trioxide, N_2O_3.

Place about one gram of arsenious acid (arsenious oxide), As_2O_3, in a test tube; add 8 cm.³ of strong nitric acid (1.30-1.35 sp. gr.) to cover the solid, then heat gently. Note the color and odor of the evolved gas, N_2O_3, as it is conducted into a test tube half filled with H_2O Is the gas soluble? Test the action of the solution on litmus paper.

Note.—It is likely that a small quantity of nitrogen tetroxide, N_2O_4, is produced simultaneously. Save the solution for use in Exp. XVI.

N_2O_3 is the anhydride of what acid? See nitrous acid. Indicate by equations the reasons for you answer.

$$(N_2,O_3) = -23{,}000 \text{ cal.}$$
$$N_2O_3 \rightarrow NO_2 + NO.$$

(*d*) Nitrogen tetroxide (nitrogen peroxide), N_2O_4 and NO_2.

Heat about 8 grams of dry lead nitrate in a test tube. Note the color and odor of the gas evolved. The vapor may be condensed in a U-tube surrounded by a freezing mixture, or a portion of it may be conducted into a concentrated solution of NaOH contained in a test tube. If all of the gas is not absorbed by the solution, test the escaping gas for oxygen. Results? What is the name of the gas? Examine the substance which remains in the ignition tube. What is it? What is the name and formula of the evolved gas? Write equations for all reactions. Keep the NaOH solution for Exp. XVII. Label it.

$$(N,O_2) = -8{,}125 \text{ cal.}$$

(*e*) Nitrogen pentoxide (nitric anhydride), N_2O_5, does not exist in the free state. It is usually prepared by distilling a mixture of phosphorus pentoxide, P_2O_5, and nitric acid. It forms colorless, rhombic prisms which are so unstable that they explode violently when heated quickly. They dissolve readily in water with the disengagement of considerable heat, forming nitric acid, HNO_3.

$$2HNO_3 + P_2O_5 \rightarrow N_2O_5 + 2HPO_3.$$
$$(N_2,O_5 - \text{gas}) = -12{,}000 \text{ cal.}$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3.$$

The series of oxides of nitrogen are an excellent illustration of what law of combination? State the law. Which of the oxides are colored? Colorless?

$$(H,N,O_3\text{—liq.}) = 41{,}500 \text{ cal.}; (H,N,O_3\text{—Aq.}) = 49{,}000 \text{ cal.}$$

From the foregoing equations it is readily seen that all of the oxides of nitrogen are endothermic compounds, i.e., the heat of formation from the elements is negative. It is obvious then, that the nitrogen oxides cannot be prepared from the elements without the addition of energy. (On account of this energy relation, the atmosphere is able to preserve its integrity as a *mixture* of nitrogen and oxygen gases, and this regardless of the heat generated by frequent electrical discharges in the atmosphere.) These endothermic oxides are unstable, and even explosive. Berthelot exploded nitric oxide by inflaming fulminating mercury.

An interesting bit of theory is associated with the thermal relations of nitrogen and oxygen. It has been ascertained that the heat of combustion of carbon or phosphorus in nitric oxide (NO) is about 21,500 calories larger than when the combustion takes place in oxygen. This is usually explained upon the theory that the energy-content of nitric oxide is greater than that of molecular oxygen (O_2). It is evident that the molecules of the gas supporting the combustion must be split into their constituent atoms. This operation will be attended by the absorption or disengagement of heat. It follows then, that less heat is required to separate NO into N and O than to separate O_2 into oxygen atoms. This is interpreted as a proof that the molecules of free oxygen, as of other elements, possess an atomic structure. That is, the negative heat of formation of nitric oxide (N,O = — 21,500 cal.) indicates that the mutual affinity of the nitrogen and oxygen atoms is less than the sum of the affinities of the oxygen atoms for themselves and the nitrogen atoms for themselves in their respective molecules.

By inspecting these same equations it will be observed at once that although the oxides of nitrogen are *formed from the elements with an absorption of heat*, the *formation of the higher oxides from nitric oxide is accompanied with a disengagement of heat.* This accounts for the readiness with which NO and N_2O_3 tend to undergo oxidation, and conversely, the easy reduction of these higher oxides to nitric oxide accounts for their marked oxidizing properties. (It will be recalled that these oxides may act as oxidizing or reducing agents. See Exp. XI.) On the other hand, nitrous oxide (N_2O) unites with oxygen to form the higher oxide, nitric oxide (N_2O,O), with an absorption of heat—therefore its slight reactivity with oxygen. Its oxidizing properties seem to be due wholly to its instability.

In concluding this note, the student is reminded that the *heat of formation* of compounds from the elements, as used in this book, is really the *heat of reaction* (see note on Energetics of Chemistry), and may be regarded not as an absolute but as a relative measure of the chemical energy of the elements of which they are composed. To illustrate by another example: Hydrogen and oxygen unite to form water as indicated by the following equation:

$$2H_2 + O_2 \rightarrow 2H_2O\text{ — gas} + 2 \times 57{,}061 \text{ cal.}$$

Interpreting the equation in the light of our theories, a definite quantity of heat will be required to split the molecules of each gas into its constituent atoms; therefore, the quantity of heat which it is possible to measure by calorimetric processes will be the true heat of union (heat of formation) less this amount. This observed heat, which is really the *heat of reaction*, merely indicates that the mutual affinity of hydrogen and oxygen is greater than the sum of the affinities of the hydrogen atoms for themselves and the oxygen atoms for themselves in their respective molecules, by an amount, the thermal equivalent of which is equal to 57,061 calories. All affinity calculations derived from thermal data by such processes must be purely relative.

Note.—The heat of dissociation of the hydrogen molecule into atoms, $H_2 \rightarrow (H,H)$, has a recorded value of 128,000 cal. (Richter.)

Experiment XII.—Preparation of Nitric Acid.

Place ten grams of pulverized sodium nitrate, $NaNO_3$ in a small tubulated retort (Fig. 37) or a distilling flask; support the retort on a wire gauze in such a manner that it can be heated conveniently. Introduce the end of the retort into a receiver (a dry test tube will do) which is immersed in cold water. Add 20 cm.³ of strong H_2SO_4 by aid of a funnel that no acid may enter the neck of the retort. Insert the stopper in the retort. Is there any evidence of chemical action taking place? Heat the retort gently and observe the gradual accumulation of liquid in the test tube. What is its color and odor? Action on litmus paper? Allow a few drops of the liquid product to run down the inside of a test tube containing a solution of ferrous sulphate, $FeSO_4$. Results? Equations? Repeat above tests using the shelf-reagent, HNO_3. Results? What is your

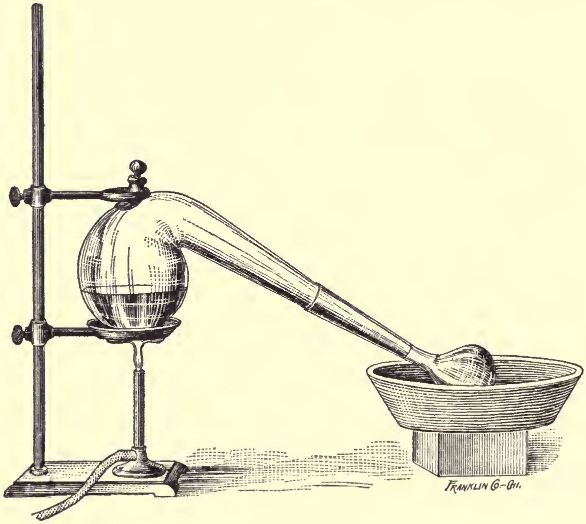


FIG. 37.

conclusion as to the identity of the liquid in the receiver? What is the substance in the retort? Write the equation for the interaction of $NaNO_3$ and H_2SO_4. Which is the more volatile, H_2SO_4 or HNO_3?

Assuming that the reaction is reversible, what is the effect of heat upon the equilibrium?

Experiment XIII.—Properties of Nitric Acid.

(*a*) Action of nitric acid on bases. To a beaker of water add a few drops of NaOH or KOH; test with red litmus paper. Now add a dilute solution of HNO_3, drop by drop, until neither blue nor red litmus paper is altered in color when dipped into the solution. Taste a drop of the solution. What has been formed by the interaction of NaOH and HNO_3? Write the "ionic" equation for the interaction.

(*b*) Oxidizing action. Test its action on indigo. Equation? Recall the action of concentrated HNO_3 on iodine. Equation? Try the action of strong boiling HNO_3 on powdered sulphur. Is there any evidence of chemical action? Dilute the solution, and test for a sulphate. Results? Equations? To a solution of ferrous chloride or sulphate add a little NH_4OH. Result? Allow contents of tube to remain exposed to the air. Results? Repeat using ferric chloride. Results? To a solution of ferrous sulphate add a few drops of concentrated HNO_3; heat gently and then add NH_4OH. Results? Explain the action of HNO_3 upon the "*ous*" salt. Equations? What property of HNO_3 which is particularly characteristic of it, is emphasized in these reactions?

(*c*) Reduction of HNO_3. Formation of ammonia. Place a few grams of zinc dust in a test tube, and add a solution of KOH (1 of KOH to 20 of H_2O). Warm the mixture gently, and test the evolved gas. What is it? Add a few drops of *dilute* HNO_3. Note the odor of the gas which is now given off. Confirm your conclusions by using two other tests. Results? Explain. Equations?

(*d*) Try the action of both dilute and concentrated HNO_3 upon each of the following metals: zinc, iron, copper, lead and tin. Note in each case the kind of gas evolved. Be on the alert for hydrogen, oxides of nitrogen and ammonia. Devise a method for showing whether the product of the reaction remaining in the test tube in each case is a nitrate or not. Apply it. Equations? Compare the interaction of HNO_3 and the metals with its action toward the non-metals. Refer to lecture notes and reference texts for assistance in balancing equations.

(*e*) Action on nitrogenous substances. Dip a quill, a piece of wool or pieces of white feather, in concentrated nitric acid. The yellow color is due to xanthoproteic acid, formed by the interaction. This is regarded as a test for nitrogen.

(*f*) Determine the relative electrical conductivity of a 5N solution of HNO_3. Results? What is its percentage of dissociation in a 1N solution? (Refer to tables.) Would you conclude that the acid is very *active* or relatively *inactive?* Why?

Enumerate several chemical properties of HNO_3 which are especially characteristic. Structural formula for nitric acid? Anhydride of the acid?

Note.—The complexities of *oxidation* by nitric acid are of such nature that the student usually requires some assistance in mastering the essential principles of the reactions involved. The principles indicated in the following equations should be thoroughly understood. The gaseous products resulting from the interaction of HNO_3 and the metals and non-metals are determined largely by the concentration of the acid.

For *dilute* nitric acid:

$$\begin{array}{c} 2HNO_3 \rightarrow 2\overline{NO} + H_2O + (3\ O) \\ S + (3\ O) + H_2O \rightarrow H_2SO_4. \\ \hline 2HNO_3 + S \rightarrow H_2SO_4 + 2\overline{NO}. \end{array}$$

For *concentrated* nitric acid:

$$\begin{array}{c} 3(2HNO_3) \rightarrow 2\overline{NO}_2 + H_2O + (O) \\ S + 3(O) + H_2O \rightarrow H_2SO_4 \\ \hline 6HNO_3 + S \rightarrow H_2SO_4 + 2H_2O + 6NO_2. \end{array}$$

Very dilute nitric acid:

$$Zn + 2HNO_3 \rightarrow Zn(NO_3)_2 + (2H)$$

$$HNO_3 + 68(H) \rightarrow \overline{NH}_3 + 3H_2O$$

or $$NH_3 + HNO_3 \rightarrow NH_4NO_3.$$

Dilute nitric acid:

$$\begin{array}{c} 2HNO_3 \rightarrow H_2O + 2\overline{NO} + (3O) \\ 3Cu + (3\ O) \rightarrow 3Cu\ O \\ 3CuO + 6HNO_3 \rightarrow 3Cu(NO_3)_2 + 3H_2O \\ \hline 3Cu + 8HNO_3 \rightarrow Cu(NO_3)_2 + 4H_2O + 2\overline{NO}. \end{array}$$

Concentrated nitric acid:

$$\begin{array}{c} 2HNO_3 \rightarrow H_2O + 2\overline{NO}_2 + (O) \\ Cu + (O) \rightarrow CuO \\ CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O \\ \hline Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2\overline{NO}_2. \end{array}$$

The *oxidation of "ous" salts to "ic" salts by means of nitric acid* may be represented by equations as follows:

$$3Fe(NO_3)_2 + 4HNO_3 \rightarrow 3Fe(NO_3)_3 + 2H_2O + \overline{NO},$$

or $$2Fe(NO_3)_2 + 4HNO_3 \rightarrow 2Fe(NO_3)_3 + 2H_2O + 2\overline{NO}_2.$$

According to the "*ion theory:*"

$$HNO_3 \rightleftarrows H^{\cdot} + NO'_3.$$

$$^*HNO_3 \rightleftarrows NO^{\cdot}_2 + OH'$$

$$HNO_3 + H_2O \rightleftarrows NO^{\cdot\cdot\cdot} + 3OH'$$

$$3Fe^{\cdot\cdot} + 6NO'_3 + \underline{NO^{\cdot\cdot\cdot} + 3OH'} + 3\underline{H^{\cdot} + 3NO'_3} = 3Fe^{\cdot\cdot\cdot} + 9NO'_3 + 3H_2O + NO.$$

or

$$2Fe^{\cdot\cdot} + 4NO'_3 + 2\underline{NO^{\cdot}_2 + OH'} + 2\underline{H' + 2NO'_3} = 2Fe^{\cdot\cdot\cdot} + 6NO'_3 + 2H_2O + 2NO_2.$$

It is obvious that *oxidation is a process whereby the number of positive charges are increased, or the negative are decreased. Reduction consists of increase of negative charges and a decrease of the positive.*

Experiment XIV.—Preparation and Properties of Aqua Regia. Oxidation of Hydrochloric Acid by Nitric Acid.

To one volume of concentrated HNO_3 add three volumes of strong HCl. Gently warm the mixture and notice its appearance and odor. This mixture

$$HNO_3 + 3HCl \rightarrow 2H_2O + N\overline{OCl} + \overline{Cl}_2,$$

of acids is usually referred to as *aqua regia* (royal water), because it will dissolve the noble metals, gold, platinum, etc., forming chlorides. No single acid with the exception of selenic acid, will dissolve gold. Place a small piece of gold leaf in each of two test tubes. To one add 2 $cm.^3$ of HNO_3, and to the other 6 $cm.^3$ of HCl. Observe that the gold leaf is not attacked. Mix the contents of both test tubes and warm gently. Results? What is formed? Equations? What is the relative solution tension of gold? (refer to table of solution-tensions). Explain the solubility of the "noble" metals in aqua regia.

Experiment XV.—Effect of Heat on Nitrates. Oxidizing Power of Nitrates.

(*a*) Recall Exp. XI (*a*). Equation? The nature of the decomposition is peculiar to ammonium nitrate.

(*b*) Recall Exp. XI (*d*). Equation? The result is typical of the nitrates of the heavy metals.

(*c*) Heat sodium nitrate in a hard glass test tube before the flame of a blast-lamp if necessary to secure an evolution of gas. Test the gas for oxygen. Continue to heat until gas is no longer evolved. What is the composition of the residue? (Do not attempt to answer this question until you have performed Exp. XVI.) The action of sodium nitrate is characteristic of the nitrates of the alkali metals and the alkali-earth metals. Keep the residue for Exp. XVI.

Note.—A residue of the same composition may be prepared more easily by melting the nitrate with a piece of lead in a crucible, and keeping

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* Ostwald, Grundriss der allgemeinen Chemie.

the mixture stirred with an iron spatula. What is action of the nitrate on the lead?

Experiment XVI.—Preparation and Properties of Nitrous Acid.

(*a*) Nitrous acid, HNO_2, is formed by the interaction of a nitrite, say sodium nitrite, $NaNO_3$, and H_2SO_4.

Add a small quantity of dilute H_2SO_4 to a dilute solution of $NaNO_2$. Test for HNO_2 as follows: Add a few drops of the mixture supposed to contain HNO_2 to a solution of KI, then add 2 cm.³ of CS_2 and shake vigorously. Free iodine proves presence of HNO_2. Equations? Prove that a nitrate will not give the same results. Record your data.

Try the action of the HNO_2 on a dilute solution of $KMnO_4$. Results? Equation? Does HNO_2 act as an oxidizer or as a reducing agent relative to KI? To $KMnO_4$?

(*b*) Test the aqueous solution of N_2O_3 prepared in Exp. XI (*c*) for the presence of HNO_2. Results? Equations? What is the anhydride of HNO_2?

(*c*) Dissolve the residue from heating $NaNO_3$ (Exp. XV) in a small quantity of water. Filter. Add dilute H_2SO_4 to the filtrate and test for the presence of HNO_2. Results? Equation? Was the residue a nitrate or a nitrite? What is the effect of heat on $NaNO_3$? Record your answer under (*c*), Exp. XV.

What class of salts are formed by the interaction of nitrous acid and the bases? Write the structural formula for HNO_2.

$$(H,N,O_2\ Aq.) = -30{,}700\ \text{cal.}$$

Experiment XVII.—Tests for Nitrates and Nitrites.

(*a*) Test for nitrates. Dissolve a small crystal of ferrous sulphate, $FeSO_4$, in 3 or 4 cm.³ of water in a test tube. Add a small quantity of the solution of any nitrate. Now hold the tube in a slanting position and carefully pour down the side 3 or 4 cm.³ of strong H_2SO_4. This should be done in such a manner that the acid may form a layer at the bottom. Notice the brown ring which forms at the boundary between the two liquids. Explain. Equation?

(*b*) Tests for nitrites. Repeat (*a*), substituting a nitrite for the nitrate. Results? Can this test be used to detect a nitrite in the presence of a nitrate, or *vice versa?* Recall the tests for HNO_2 (nitrite) used in Exp. XVI. These tests will enable you to detect a nitrite in the presence of a nitrate, but the nitrite must be removed before (*a*) may be applied as a test for the nitrate. This is usually accomplished by boiling the solution with NH_4Cl. See Exp. I for the reaction.

The tests are usually carried out as follows: 3 or 4 cm.³ of the "unknown" solution are placed in a test tube, acidulated with dilute H_2SO_4, and tested for a nitrite, using the KI or the $KMnO_4$ test. If a nitrite is absent, the solution is tested at once for a nitrate; but if a nitrite is present, a portion of the "unknown" solution is boiled with NH_4Cl until small portions of the solution which are removed, give no test for the nitrite. The test for nitrates is then applied.

(*c*) Prepare a solution containing a nitrite and a nitrate and proceed with the analysis as per directions. Record all data.

(*d*) Test the NaOH solution of N_2O_4 prepared in Exp. XI (*d*), for nitrates and nitrites. Results? What do you infer was the action of the N_2O_4 on the NaOH solution?

All nitrates and nitrites are soluble in water. The silver salt of nitrous acid is sufficiently difficult of solution to be precipitated on the addition of silver nitrate to a solution of a nitrite if the latter is not too dilute.

PHOSPHORUS, P.

At. Wt. 31 Mol. Wt. (P_x–P_4).

Phosphorus, like sulphur, exists in several allotropic forms—*crystalline* or *yellow* phosphorus, and *amorphous* or *red* phosphorus. The properties of these forms differ widely although they are composed of the same materials. However, their respective energy-contents are very different. —See "Note on the Energetics of Chemistry."

$$\text{(Yellow) P} \longrightarrow \text{(Red) P} = 27{,}300 \text{ cal.}$$

The approximate thermal equivalent of the difference between the intrinsic energies of the allotropic forms is 27,300 cal.

Experiment I.—Properties of Phosphorus.

Caution.—Yellow phosphorus must be kept and cut under water. It must be handled with forceps, never with the fingers.

Determine the physical properties of the *yellow* and *red* varieties of phosphorus. Place a quantity of powdered boneblack upon an iron plate (tile or brick). Lay a piece of yellow phosphorus about the size of a pea upon this and heap the powder up around the phosphorus, but leave the top of the phosphorus exposed to the air. Does the phosphorus take fire? Explain. Equations? Repeat the experiment using red phosphorus. Results? Explain.

Determine the relative solubility of the two forms of phosphorus in CS_2. Results? Dissolve a very small piece of yellow phosphorus in about 1 $cm.^3$ of CS_2. Place a filter paper on the ring of the ring-stand; pour the solution upon the filter paper. Let the CS_2 evaporate without heating. Result? Equation?

Prove that yellow phosphorus is practically insoluble in water or alcohol.

Drop a small piece of yellow phosphorus into a flask half filled with water. Heat the flask until the phosphorus is melted, then pass a current of oxygen through a delivery tube upon the melted phosphorus in the bottom of the flask. Results?

Put a drop of liquid bromine in a dry bottle; allow the bromine to vaporize. When the bottle is filled with the vapor, throw a small dry piece of yellow phosphorus into the bottle (?). Equation? Is the product stable? Repeat, using red phosphorus (?).

Bring together in a porcelain crucible or an evaporating dish a flake of iodine and a very small dry piece of yellow phosphorus (?). What is the source of the light and heat? Equation? Is the product stable? Does red phosphorus yield similar results?

Place a small quantity of red phosphorus in the bottom of a test tube. Clamp the tube in a horizontal position, and *gently* heat the end containing the phosphorus. What is the *yellow* substance which collects on the cold portion of the tube? Verify your conclusion by suitable tests. Did the red phosphorus melt or *sublime?*

Tabulate in vertical columns against one another the corresponding properties of these two modifications of phosphorus. To what is this difference of behavior attributed?

Hydrogen Derivatives.

Experiment II.—(Hood) Preparation of Phosphine.

(*a*) Into a beaker nearly full of water (a few drops of HCl will increase the speed of the reaction) drop a small piece of calcium phosphide, Ca_3P_2 (?). Equation? Recall the action of magnesium nitride, Mg_3N_2, upon water.

Note.—Calcium phosphide has an irregular composition, and because of this fact, a mixture of the three hydrides, PH_3, P_2H_4, P_4H_2 is obtained. Which of the three inflames spontaneously in the air and gives to gaseous phosphine its spontaneous inflammability? By what other names is gaseous phosphine known?

(*b*) A small generating flask (100–250 cm.³) is fitted with a rubber stopper provided with two right-angled delively tubes, *a* and *b* (Fig. 38). A short piece of rubber tubing, carrying a pinch cock is attached to *a*. In the flask, place a strong solution of KOH (1 of KOH to 2 of H_2O). The flask should be half filled, then place it on a piece of iron gauze supported on the ring stand in such manner that the flask may be heated. Connect *b* with a delivery tube bent so that its lower end, which is turned upward, dips beneath the surface of water in a large beaker or a pneumatic trough. The water should have a temperature of about 20°. Now drop a piece of phosphorus about the size of a pea into the flask and stopper, air-tight. Connect *a* with a hydrogen generator and pass a current of hydrogen through the apparatus until all of the air is displaced; disconnect from the generator and close pinch cock on *a*. (A current of coal gas may be used instead of the hydrogen, or a few drops of ether may be added to

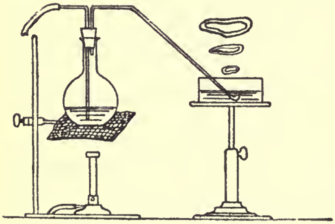


FIG. 38. (*Smith and Keller.*)

the contents of the flask. The ether on evaporating will drive the air out of the flask.) Heat the flask gently and phosphine will be evolved (?). Equation? What is formed by the burning of the phosphine? Equation?

Caution.—Do not remove the lamp or the tube from the water until the reaction has terminated, then lift tube from water first, and remove the lamp. The gas is poisonous.

Read "Note" in (*a*) if you have not already done so. Is there any similarity between ammonia and phosphine?

$$\text{(Yellow) } P + 3H \longrightarrow PH_3 + 11{,}600 \text{ cal.}$$

Phosphorus and the Halogens.—We have seen that the halides of phosphorus may be formed by the direct union of the elements. The halides, being exothermic compounds, are very much more stable than the analogous compounds of nitrogen. In contact with water they are unstable, undergoing hydrolysis, with the formation of a hydrogen halide and an oxacid of phosphorus. The reactivity of the halides of phosphorus with water is fully explained by the large amount of heat liberated at the time of the action.

$(P,Cl_3) = 75{,}300$ cal. $(P,Cl_5) = 104{,}900$ cal.
$(P,Br_3) = 42{,}600$ cal. $(P, I_3) = 10{,}900$ cal.

Experiment III.—Decomposition of the Halides of Phosphorus by Water. Hydrolysis.

(*a*) Preparation of phosphorous acid by hydrolysis of phosphorus trichloride. Place a few drops of phosphorus trichloride, PCl_3, in a test tube; blow your breath across the mouth of the test tube (?). Recall the test for a hydrogen halide. Now add a small quantity of water to the oily liquid (?). Ascertain whether any thermal phenomena accompanies the dissolving of the PCl_3 or not (?). Warm the tube, and again blow your breath across its mouth (?). What are your inferences? Equations? Evaporate the solution to dryness on a water-bath until all of the HCl has passed off. What is the residue? Add a little water to the residue and try the effect of the solution upon a $AgNO_3$ solution. A black precipitate proves the presence of phosphorous acid, H_3PO_3.

(*b*) Preparation of phosphoric acid by hydrolysis of phosphorus pentachloride.

By means of a spatula, place a small quantity of PCl_5 in a test tube. Blow your breath across the mouth of the tube (?). Add a few cm.^{3} of water. Note the hissing noise which accompanies the reaction. Is the test tube warmed by the interaction of the substances? Warm the tube and again blow your breath across its mouth (?). Test it with litmus paper (?). Boil until the solution is free of HCl. What is the remaining fluid? Add a few drops of it to a $AgNO_3$ solution (?). A yellow precipitate of silver orthophosphate, Ag_3PO_4, proves the presence of phosphoric acid, H_3PO_4. Equations?

Recall the methods used for the preparation of pure hydriodic and hydrobromic acids.

Oxygen Derivatives.

Experiment IV.—Preparation and Properties of Phosphorus Pentoxide. Phosphoric Acid.

Burn a carefully dried piece of phosphorus under a bell-jar. Allow the jar to remain undisturbed until the heavy white vapors have deposited upon its sides. Compare the white powder with the substance labeled "phosphorus pentoxide," P_2O_5. Place a portion of each in separate test tubes containing a little water (?). Is there any thermal evidence of chemical action? Test each with litmus paper (?). Compare their actions toward a silver nitrate solution (?). When phosphorus burns with a free supply of oxygen, what compound is formed? Formula? When this compound reacts with water, what is the product? Equation? Name two other oxides of phosphorus and give the formula for each. What is the anhydride of phosphoric acid? Of phosphorous acid?

$$(P_2,O_5) = 369{,}800 \text{ cal.} \qquad (P_2O_5, \text{Aq.}) = 41{,}600 \text{ cal.}$$

Phosphorus pentoxide is one of the most effective drying agents known. It has been shown that a glass tube, four or five inches in length, filled with the phosphorus pentoxide, will entirely dry a gas which is slowly passing through.

Experiment V.—Preparation and Properties of Phosphoric Acid.

Phosphoric acid may be prepared by heating a very small quantity of red phosphorus with an excess of strong nitric acid; filter and remove excess of water by evaporation on the steam bath. The thick syrup which remains should be dissolved and tested for phosphoric acid with a silver nitrate solution (?).

What is the formula for phosphoric acid? How many replaceable hydrogen atoms? Is it unibasic, dibasic or tribasic? Into what ions does it dissociate when placed in water. Is it a "strong" acid? (Refer to tables.) State the reasons for your answer. Write the structural formula for phosphoric acid. Give the names and formulæ of three other acids of phosphorus.

From data given in Exp. IV calculate the "heat of formation" of phosphoric acid in aqueous solution from its elements.

Experiment VI.—Reactions of the Orthophosphates.

(*a*) Dissolve a little disodium hydrogen orthophosphate, Na_2HPO_4, in water. Test a portion of the solution with litmus paper (?). Explain.

(*b*) To this portion add silver nitrate in solution (?). Filter. Ascertain the solubility of the yellow precipitate in HNO_3 (?). In NH_4OH (?). Equations?

(*c*) Test a portion of the original solution with ferric chloride, $FeCl_3$ (?). Add sufficient HCl to dissolve the precipitate, then add slowly NH_4OH until the solution is alkaline (?). Equations?

(*d*) Test a solution of any soluble orthophosphate with "magnesia mixture" (?). Is the precipitate crystalline?* Is the precipitate soluble in excess of $MgSO_4$? Is it reprecipitated in the *cold* by NH_4OH? Equations?

Note.—"Magnesia mixture" is prepared by adding a little NH_4OH and an excess of NH_4Cl to a solution of magnesium sulphate, $MgSO_4$.

(*e*) Add an ammonium molybdate, $(NH_4)_2MoO_4$, solution to a dilute solution of an orthophosphate acidified with concentrated HNO_3 (?). Describe the precipitate. What is it? Give the formula. Equations?

Note.—(*d*) and (*e*) are reactions frequently employed in analytical chemistry.

Experiment VII.—Preparation and Reactions of the Pyrophosphates.

When disodium hydrogen orthophosphate, Na_2HPO_4, is heated to about 300°, each two equivalents of it evolve one equivalent of water and a neutral *sodium pyrophosphate* is formed as a colorless glassy mass, soluble in water.

Place a small quantity of Na_2HPO_4 in a crucible and heat to redness (?). Equations? Dissolve the glassy residue (?) in water and test the solution as per Exp. VI., (*a*), (*b*), (*c*), (*d*), (*e*). Tabulate results. Equations?

Test a solution of $H_4P_2O_7$ (or a pyrophosphate acidified with acetic acid) with a clear solution of albumen. Is the latter coagulated?

Experiment VIII.—Preparation and Reactions of the Metaphosphates.

(*a*). Heat to redness a little microcosmic salt (sodium ammonium hydrogen orthophosphate, $NaNH_4HPO_4$), and dissolve the residue of sodium metaphosphate in water. Test the solution as per Exp. VI., *a*, *b*, *c*, *d*, *e*. Tabulate results. Equations?

Test a solution of HPO_3 with a clear solution of albumen. Is the latter coagulated?

(*b*) Bend the end of a platinum wire into a closed loop; heat it to redness, then plunge it into a little microcosmic salt; heat strongly in the outer zone of the blow-pipe flame until a "glassy bead" forms (?). Touch the hot bead to some powdered CuO and heat strongly again. If the operation has been successful a clear blue-green bead will be formed. The solubility of certain metallic oxides in the metaphosphates and the metaborates is taken advantage of to detect their presence. The color of the bead is characteristic of the oxide.

---

*If the precipitate formed above is not crystalline add a slight excess of HCl and reprecipitate with very dilute NH_4OH.

Experiment IX.—Tests to Distinguish the Phosphates.

Mention one reaction which will enable you to distinguish orthophosphates from all other phosphates. Try it. Record method and results. How would you distinguish between a meta- and a pyrophosphate? Try it. Record all data.

With the exception of members of the potassium family, the normal orthophosphates and pyrophosphates of all the metals are insoluble in water.

ARSENIC, AS.

At. Wt. 75.0 Mol. Wt. (As_2, 645°–As_4, 1,700°).

Arsenic is essentially an acid-forming element and is, therefore, a non-metal. In some of its compounds, however, it functions apparently as a metal. It cannot displace hydrogen from dilute acids. It has valences of three and five.

Experiment I.—Properties of Arsenic.

(*a*) Study the physical properties of the elementary substance. Does it possess a metallic appearance? Is it crystalline in form? Place a piece of arsenic about half the size of a grain of wheat in a small tube of hard glass and heat to redness (?). What name is applied to such change of state? Repeat using orpiment, As_2S_3, or realgar, As_2S_2.

(*b*) Heat a very small piece of arsenic on charcoal in the oxidizing flame. Results? Note that the characteristic odor of garlic is perceptible. Will the free element burn in the air? If so, what is formed?

(*c*) To a small quantity of arsenic in a test tube add an excess of HNO_3. Boil so long as brown fumes form, or until the liquid does not color on cooling. Save the solution for use in Exp. V.

Recall similar experiments with iodine and phosphorus (?).

Hydrogen Derivatives.

Experiment II.—Arsine. Marsh's Test for Arsenic.

(Hood; Poison! Instructions). Thoroughly clean the hydrogen-generator; place a small quantity of *chemically pure* zinc in the flask; connect the generator with a tube (U-tube or bulb-tube) filled with calcium chloride, $CaCl_2$. Connect this latter tube with a piece of hard glass tubing, *r*, about 20 cm. long, clamped in a horizontal position (Fig. 39). It is well to make constrictions in the tube at intervals of 7 or 8 cm. by gently heating and drawing it out. Now add dilute HCl through the thistle tube. When the air has been displaced by hydrogen, light the gas by the "test tube" method. Observe the color of the flame. By means of a pair of pinchers hold a porcelain crucible lid in the flame. If there is no deposit of solid matter upon the lid, introduce through the thistle tube a few drops of a solution of arsenic trichloride (arsenic trioxide, As_2O_3, dissolved in HCl).

Note the appearance of the flame (?). Is there a deposit upon the cold porcelain lid? Marsh's test: Heat the horizontal tube between any two constrictions, with a flame. Results? Locate the deposit in the tube relative to generator and the flame. Has the deposit upon the lid a metallic luster? Test the solubility of the deposit (arsenic "spot") with any soluble hypochlorite. Indicate by equations the chemical reactions involved in the preparation of the gas, *arsine*. Explain by use of equations the changes occurring within the flame. What other name is sometimes applied to the gas, AsH_3?

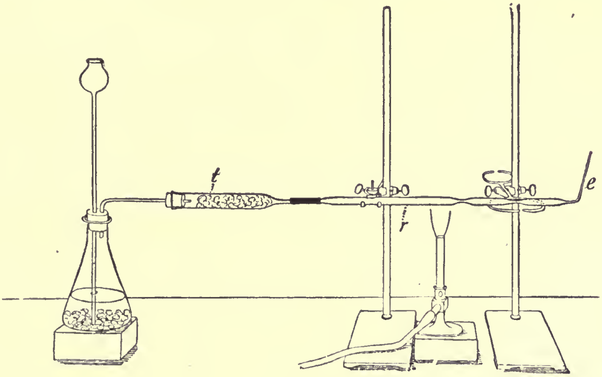


FIG. 39.

Note.—The student may be asked to determine whether or not arsenic is present in the green coloring matter used on wallpaper and shipping-labels.

$$As + H_3 \longrightarrow AsH_3 \quad -11,700 \text{ cal.}$$

Oxygen Derivatives.

Experiment III.—Arsenic Trioxide (Arsenious Oxide). Arsenious Acid.

(*a*) Place a little powdered arsenic in a hard glass tube open at both ends and about 20 cm. long. Clamp the tube in a nearly horizontal position and heat. Notice the white deposit of arsenic trioxide, As_2O_3, on the colder portions of the tube. Scrape the deposit into a small test tube and resublime it. Does the sublimate show a crystalline structure? By what other name is arsenic trioxide commonly known?

$$(As_2, O_3) = 154,600 \text{ cal.}$$
$$(As_2, O_5) = 219,400 \text{ cal.}$$

(*b*) Reduction of arsenic trioxide. Heat a pinch of As_2O_3 after mixing it with a little powdered wood charcoal, in a very narrow test tube (or, better, in a drawn-out glass tube having a small bulb on the end). Results? Equation?

Note.—It is advisable to cover the mixture with a layer of powdered charcoal.

(*c*) Preparation of arsenic trichloride. Boil a small quantity of As_2O_3 with concentrated HCl (?). Equation? Add a few cm.³ of water. Preserve the solution for future use. Does As_2O_3 in this reaction manifest the properties of a metallic or a non-metallic oxide, i.e., *basic* or *acidic* properties?

$$(As, Cl_3) = 71,400 \text{ cal.}$$

(*d*) Preparation of sodium arsenite, Na_3AsO_3. Boil a small quantity of As_2O_3 with a solution of sodium hydroxide. Results? Equation?

Does As_2O_3 in this reaction manifest the properties of a metallic or a non-metallic oxide?

(*e*) Formation of arsenious acid, H_3AsO_3. Heat a little As_2O_3 in 10 cm. of distilled water in a test tube. Filter if the solution is not clear. Test the action of the filtrate upon litmus paper (?). Conclusions? As_2O_3 is the anhydride of what acid? Ascertain the solubility of As_2O_3 in water by evaporating a portion of the solution to dryness (?). The names of the salts formed by this acid have what ending? Is H_3AsO_3 known in the free state? What is the best antidote for arsenious oxide? Write the structural formula for arsenious acid.

Experiment IV.—Salts of Arsenious Acid.—Arsenites.

(*a*) To a portion of a solution of sodium or potassium arsenite add a little silver nitrate solution (?). Filter. Try the effect of an excess of NH_4OH upon a portion of the precipitate (?). Boil (?). What is the effect of HNO_3 upon the precipitate? Equations?

(*b*) Add a few cm.³ of a solution of copper sulphate to a portion of the aqueous solution of the arsenite (?). Is the precipitate soluble in NaOH? Heat the solution (?). Equations?

Experiment V.—Arsenic Acid.—Arsenates.

Note.—The student should be on the alert to trace any analogies of crystalline form, composition, solubility, etc., of the phosphates and arsenates.

(*a*) Evaporate the solution of arsenic in nitric acid, Exp. I (*c*), to dryness and redissolve the residue in 20 cm.³ of hot water. The purpose of this operation is to remove any free HNO_3. Test the solution with litmus paper (?). Is the acid reaction due to nitric acid or arsenic acid, H_3AsO_4? Arsenic acid may be prepared by substituting As_2O_3 for the metallic arsenic and following the foregoing procedure. Equations?

(*b*) Precipitation of silver orthoarsenate. Add a slight excess of $AgNO_3$ solution to 5 cm.³ of the arsenic acid solution (?). Filter. Try the solubility of separate portions of the precipitate in NH_4OH (?), and in

HNO_3(?). What is the effect of boiling the NH_4OH solution? Equations?

(*c*) Precipitation of magnesium ammonium orthoarsenate. To "magnesia mixture" containing an excess of NH_4OH, add 5 cm. of the solution of H_3AsO_4 (or any soluble *arsenate*) (?). If the precipitate is not crystalline dissolve it in the smallest quantity of HCl, and reprecipitate it with NH_4OH. Equations?

(*d*) Precipitation of ammonium arseno-molybdate. Add an ammoniun molybdate solution to 5 cm.^{3} of the H_3AsO_4 solution (or any soluble arsenate) acidified with concentrated HNO_3 (?). If precipitation is apparently incomplete, warm the mixture (?). Equations? Name and give the formulæ of four acids of arsenic. Into what ions does arsenic acid dissociate when placed in water? Is it a "strong" acid? (Refer to tables.) Write the structural formula for the acid.

Experiment VI.—(Optional) Reactions of the Orthoarsenates.

Exp. VI.—"Phosphorus," may be repeated using any soluble arsenate instead of Na_2HPO_4. Equations?

Experiment VII.—Sulphides of Arsenic. Colloidal Solutions. Sulpo-salts.

(*a*) Precipitation and properties of arsenic trisulphide. Pass H_2S into a solution of H_3AsO_3 (or of an arsenite) (?). What name is applied to this kind of a solution?

Pass H_2S into the solution of As_2O_3 in HCl prepared in Exp. III (*c*), (or of an arsenite acidified with HCl) (?). Filter and wash the precipitate. Divide the precipitate into two parts. Boil one portion with dilute HCl. Is the precipitate apparently soluble? Place the other portion of the precipitate in an evaporating dish and add few cm.^{3} of warm ammonium sulphide, $(NH_4)_2S$, or warm ammonium polysulphide, $(NH_4)_2S_x$ (?). Add HCl to the solution thus formed and note the effect? Equations?

(*b*) Precipitation and properties of arsenic pentasulphide. Repeat (*a*), substituting H_3AsO_4 (or an arsenate) for the H_3AsO_3.

Experiment VIII.—Tests for Arsenic.

In addition to *Marsh's test*, the following tests are used for the detection of arsenic: Reinsch's, Bettendorff's, Gutzeit's, Fleitmann's. Consult works on analytical chemistry and make a detailed statement of one of the above methods. Test the method before reporting. The method may be presented in the form of a record of your experiment.

ANTIMONY, Sb.

At. Wt. 120. 2 Mol. Wt. (Sb_2–Sb_4).

The metallic characteristics exhibited by arsenic become more marked with **antimony**. It is both an acid-forming and base-forming element.

It is a weak "metalloid." It gives sets of compounds in which it is trivalent, and others in which it is quinquivalent. It cannot displace hydrogen from dilute acids.

Experiment I.—Properties of Antimony.

Note.—The chemical properties of antimony are very similar to those of arsenic.

(*a*) Study the physical properties of the elementary substance. Does it possess a metallic appearance? Is it crystalline? Heat a small piece of antimony to redness in a hard glass tube closed at one end (?). Repeat the experiment using a tube open at both ends (?).

(*b*) Heat a small piece of antimony on charcoal in the oxidizing flame. Results? Will the free element burn in the air? If so, what is formed?

(*c*) Boil a little powdered antimony in concentrated HNO_3. Results? Preserve for use in Exp. IV.

Hydrogen Derivatives.

Experiment II.—Stibine. Test for Antimony.

Repeat Marsh's test, using antimony trichloride, $SbCl_3$, in HCl solution in place of $AsCl_3$. Distinguish between arsine and stibine.

Note.—The student may be asked to prove *experimentally* that tartar emetic contains antimony. What is the formula of this salt?

$$Sb + H_3 \rightarrow SbH_3 - 84{,}500 \text{ cal.}$$

Halides.

Experiment III.—Hydrolysis of Antimony Trichloride. Mass Action.

(*a*) Recall Exp. II. "Chlorine." Equation?

(*b*) Place a small crystal of antimony chloride, $SbCl_3$, in a test tube. Add 10 cm.^{3} of water and shake (?). Test the liquid with litmus paper (?). Prepare a clear solution by adding concentrated HCl, a drop at a time, warming the mixture after each drop. The solution contains what? To 5 cm.^{3} of the solution add a large amount of water. Result? Explain. What kind of action is this? Write the equation for the reaction.

Now add concentrated HCl. Result? Is the action reversible? What influences the direction of the reaction? Write an equation which will represent both actions. Referring to your equation, in which direction does the reaction go with the greatest speed when an excess of acid is used? When an excess of water is used?

$$(Sb,Cl_3) = 91{,}400 \text{ cal.}$$

Oxygen Derivatives.

Experiment IV.—Antimony Trioxide. Antimony Pentoxide.

Examine the residue which remained in the tube after heating powdered antimony with HNO_3 (Exp. I, (*c*)). The white insoluble residue is probably a mixture of antimony tri- (Sb_2O_3) and penta- (Sb_2O_5) oxides of antimony. These oxides are the anhydrides of what acids? Filter the solution and boil a small portion of the residue with a solution of NaOH until a clear solution is obtained. Products? Does the oxide exhibit acid or basic properties in this reaction? Equation?

Boil another small portion of the residue with strong HCl. Products? Would you infer from this reaction that the oxide of antimony possesses basic properties? Why? Evaporate the clear solution to small bulk. Does it interact with water like $SbCl_3$? Save a portion of the clear solution for Exp. V.

$$(Sb_2, O_3, 3H_2O) = 167{,}400 \text{ cal.}$$
$$(Sb_2, O_5, 3H_2O) = 228{,}700 \text{ cal.}$$

Experiment V.—Sulphides of Antimony. Sulpho-salts.

Into a solution of $SbCl_3$ acidified with HCl pass H_2S (?). Equation? Filter and wash the precipitate. Divide the precipitate into two parts. To one portion add strong HCl. Warm. Result? Equation? Try the action of warm $(NH_4)S_x$ upon the other portion of the precipitate (?). Equation? To the solution add HCl (?). Is Sb_2S_3 soluble in $(NH_4)_2S_x$? What salt is formed? Equations?

BISMUTH, Bi.

At. Wt. 208.0 Mol. Wt. (Bi–Bi_2).

The metallic character of **bismuth** considerably exceeds its metalloidal properties. It does not form a hydrogen derivative, and the oxide (Bi_2O_3) which possesses a constitution similar to the acid forming As_2O_3 exhibits only basic characteristics. Bismuth and its derivatives are usually considered with the metals, but on account of the fact that it forms a number of compounds analogous in composition and properties to the compounds of other members of the group, it is considered in this order.

Experiment I.—Properties of Bismuth.

(*a*) Note the physical properties of the elementary substance (?). Is it malleable or brittle. (Test with the pestle.)

(*b*) Heat a small piece of bismuth on charcoal in the oxidizing flame. Results?

(*c*) Mix a little oxide or nitrate of bismuth with a small quantity of sodium carbonate, Na_2CO_3. Heat the mixture on charcoal in the reducing flame. Examine the resulting metallic globule (?). Explain. Equation?

(*d*) Treat a pinch of powdered bismuth with HNO_3. Result?

Products? Concentrate the solution, cool and crystallize. Save for Exp. III.

Experiment II.—Alloys. Wood's Metal.

Place a small piece of Wood's metal (an alloy) in a small test tube. Support the test tube in a beaker of water; heat the water in the beaker. Determine the temperature at which the alloy melts by taking the temperature of the water-bath (?). Name the components of the alloy and give their respective melting points.

Experiment III.—Hydrolysis of Bismuth Nitrate.

Dissolve the crystals prepared in Exp. I (*d*), (or crystals of bismuth nitrate, $Bi(NO_3)_3$) by heat with the addition of the least possible amount of nitric acid. To a few cm.^{3} of the solution add a large quantity of water. Result? Add a few drops of dilute HNO_3, just enough to remove the cloudy appearance (?). Add a large volume of water (?). Explain. Equations? Is the action reversible?

Experiment IV.—Preparation of Bismuth Hydroxide. Dehydration. Bismuth Trioxide.

(*a*) Try the effect of NH_4OH upon a clear solution of $Bi(NO_3)_3$. Result? What are the products? Equation? Filter and wash the precipitate.

(*b*) Remove the precipitate from the filter and place it in a porcelain crucible. Ignite. Note the color of the residue of bismuth trioxide when hot; also cold (?). Equation? Define dehydration.

$$(Bi_2,O_3) = ?\text{ cal.}$$

Experiment V.—Preparation of Bismuth Trichloride. Hydrolysis.

Pour a few drops of dilute HCl upon precipitated $Bi(OH)_3$ upon a filter (?). Collect the filtrate in a test tube containing 15 to 20 cm.^{3} of water. Result? Explain. Equation? The halide of what other element manifests a tendency to undergo hydrolysis?

$$(Bi,Cl_3) = 90{,}600\text{ cal.}$$

Experiment VI.—Bismuth Trisulphide.

Pass H_2S through a solution of the chloride or nitrate of bismuth containing just enough HCl to prevent hydrolysis. Result? Products? Equation? Filter and discard the filtrate. Treat the precipitate with warm $(NH_4)_2S_x$. Is the precipitate apparently soluble? Filter and add HCl to the filtrate. Is the yellowish-white substance free sulphur or bismuth trisulphide, Bi_2S_3? Is Bi_2S_3 soluble in $(NH_4)_2S_x$? Equations? Compare results with those in Exp. V. "Antimony" (?).

The following comparative table will show that the elements of the nitrogen family exhibit the same gradation of properties with increasing atomic weights as was displayed by the elements of the oxygen family:

Physical Properties	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic weight.....	14.01	31.0	75.0	120.2	205.0
State or phase......	Gas	Solid (crystalline)	Solid (crystalline)	Solid (crystalline)	Solid (crystalline)
Color	Colorless	Yellow	Steel-gray	Silver-white	Reddish, Metallic.
Specific gravity.....	.886 (liquid)	1.82	5.72	6.7	9.8
Specific heat.......	< ——	——	——	——	—— <
Melting-point......	—213°	44°	450°	425°	270°
Boiling-point..... .	—193°	287°	800°	1,400°?	1,600°?
Chemical properties					
H-derivatives......	NH_3	PH_3	AsH_3	SbH_3	......
Heat of formation..	11,800 cal.	11,600 cal.	—11,700 cal.	—84,500 cal.	......
Chemical properties	Strong base	Weak base	Neutral	Neutral	......
Halides............	NCl_3	PCl_3	$AsCl_3$	$SbCl_3$	$BiCl_3$
Heat of formation..	—38,100 cal.	75,000 cal.	71,400 cal.	91,400 cal.	90,600 cal.
State or phase......	Liquid	Liquid	Liquid	Solid	Solid
Stability	Explosive	Decomposed by water	Decomposed by water	Undergoes hydolysis	Undergoes hydrolysis.
O-derivatives	N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
and	N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5.
Chemical properties	Anhydrides	Anhydrides	Anhydrides	Weak anhydrides, basic.	Strongly basic.
Acids	HNO_2	H_3PO_3	H_3AsO_3	$HSbO_2$	......
	HNO_3	H_3PO_4	H_3AsO_4	H_3SbO_4	......
Metallic properties.	> ——	——	——	——	—— >

PROBLEMS.

1. If a liter of water absorbs 800 times its volume of ammonia gas, how many grams of ammonia will be absorbed by 500 cm.^{3} of water?
2. How many grams do 100 cm.^{3} of concentrated HNO_3 weigh?
3. How many grams of concentrated HNO_3 can be made from 10 grams of sodium nitrate?
4. How much phosphorus can be obtained from 100 grams of bone-ash, containing 75 per cent. of calcium phosphate, $Ca_3(PO_4)_2$? From 100 grams of pure apatite, $Ca_5F(PO_4)_3$?
5. Calculate the percentage of arsenic in realgar. In orpiment.
6. The specific gravity of the vapor of phosphorus relative to hydrogen (H_2) is 119.8 at 800°. How many atoms in the molecule of the elementary substance?
7. Specific gravity of vapor of arsenic at 900° is 296.6; at 1740°, 154.6. Determine the molecular formula of arsenic at the respective temperatures.

CHAPTER XX.

CARBON FAMILY.

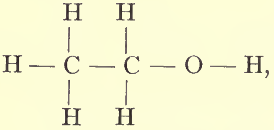
Carbon	C,	12.00
Silicon	Si,	28.4
(Germanium	Ge,	72.5)
(Tin	Sn,	119.0)
(Lead	Pb,	206.9)

The first two elements of this family are entirely non-metallic, while the others are metals exhibiting properties, however, which reveal resemblances to the non-metals. The group, for advantage of study, may be and is frequently divided into a *primary group* including carbon and silicon, and a *secondary group* composed of germanium, tin and lead. All of the elements of the family possess a maximum valence of four. They unite with four atoms of hydrogen or of the halogens. With the exception of silicon, they also form compounds in which they are bivalent.

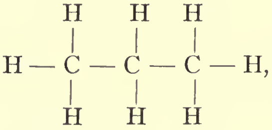
PRIMARY GROUP.

Carbon and **silicon** resemble one another in their chemical conduct. Some of their physical properties are quite similar. Their derivatives are also very much alike—the halogen compounds exhibiting similar properties, the oxides being weak acid anhydrides which are capable of forming stable salts with bases. The acids of carbon and silicon are unstable, decomposing into water and the acid anhydride. The normal valence of the two elements is four.

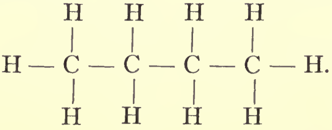
The essential difference in the chemical conduct of carbon and silicon is the ability of atoms of the former to combine with each other and form "chain compounds," i.e., carbon possesses the property of satisfying its own bonds of valence. This property is indicated in the following structural formulæ of ethyl alcohol (C_2H_5OH), propane (C_3H_8), and butane (C_4H_{10}):



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H, \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H, \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H. \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

Silicon does not possess the power of satisfying its own bonds, consequently it does not form "chain compounds."

CARBON, C.

At. Wt. 12.00 Mol. Wt. (C_x).

Carbon occurs in the *free* and almost pure state in nature in several *allotropic forms* known as *diamond*, *graphite* or *plumbago* and *amorphous* carbon. It is also found in the *combined* condition in all living things, in carbon dioxide and carbonates, in turf, peat, lignite or brown coal, bituminous coal and anthracite coal, and in such mineral oils as asphaltum and petroleum. As the result of the power of carbon to satisfy its own bonds, the number of possible carbon compounds is so large that it appears necessary, for purposes of convenience, to treat them apart in a separate portion or special phase of chemistry. With hydrogen carbon forms practically an unlimited number of compounds into which nearly all other elements, especially oxygen, nitrogen, the halogens and sulphur can enter. The derivatives of carbon have been termed *organic compounds* because of the idea which prevailed for many years, that these compounds could not be produced without the intervention of life, i.e., that their artificial production was impossible. On account of this original belief the chemistry of the carbon compounds is commonly known as *organic chemistry.*

Although it is true that a large number of the derivatives of carbon are obtained exclusively from animal and vegetable organisms, yet many of them are prepared artificially from simpler ones or from the elements by simple *synthetic* methods. The student is also reminded of the fact that hundreds of definite chemical compounds, including drugs and dyes of great value, apparently unknown to either animal or vegetable life, have been prepared artificially. The preparation of many other compounds is delayed solely because of their unusual complexity and instability.

Experiment I.—Properties of Carbon.

(*a*) Enumerate the known allotropic modifications of this element. Examine specimens of each. Which represents the purest carbon? Tabulate their principal physical properties?

(*b*) Preparation of amorphous carbon.

(*b*1) Place about 1 gram of cane sugar ($C_{12}H_{22}O_{11}$) in an old test tube and heat until vapors cease to appear. Was water liberated during the process? Pulverize the black residue in a mortar. What is it? Equation?

(*b*2) Cover the bottom of a crucible, preferably an iron crucible provided with lid and delivery tube, with sand. Place a number of small pieces of soft pine (largely cellulose, $(C_6H_{10}O_5)_n$ in the crucible and cover with sand to partially exclude the air. Support the crucible in a pipe-stem or wire triangle and heat for about a half-hour or until the contents of the crucible cease to smoke. Allow the crucible to cool, then pour the contents out upon an iron plate. Place one or two of the *charred* pieces of wood in a mortar. It should reduce readily to a fine powder. What is it? Equation?

(*b*3) Close the holes at the bottom of a lighted Bunsen burner and hold a piece of cold glass tubing in the upper portion of the flame. What is the black deposit? By what two names is it known?

Repeat, using the flame of a candle (?).

(*b*4) (Hood). Apply a flame to a piece of camphor gum ($C_{10}H_{16}O$) about the size of a pea. Does it burn with a "sooty" flame? Explain.

(*b*5) Name the different kinds of charcoal. Give an example of "destructive distillation," and define same. What is boneblack? Coke?

(*c*) Porosity of charcoal. Observe that a piece of ordinary charcoal floats upon the water. Place a small piece of it in a test tube half full of water; by means of a long glass rod or a piece of wire force the charcoal down to the bottom of the tube and boil the water for several minutes or until the charcoal shows little or no tendency to float. Explain.

(*d*) Decolorizing action of charcoal. To a test tube one-fourth full of powdered animal charcoal add 10 $cm.^3$ of water which has been colored by the addition of a few drops of an indigo solution or a litmus solution; shake thoroughly for a few minutes, then heat to boiling; filter through a wet filter paper and compare the filtrate with that of the original solution (?). Explain.

Note.—A solution of brown sugar may be substituted for either of the above solutions.

(*e*) Deodorizing action of charcoal. Fill a test tube nearly one-third full of powdered charcoal; add 5 $cm.^3$ of a weak solution of hydrogen sulphide; cork the tube tightly and shake vigorously; set the tube aside and after fifteen to thirty minutes note the odor of the contents (?). Repeat until your results are definite. Explain.

(*f*) Reducing action of charcoal. Mix thoroughly on a piece of paper 2 grams of copper oxide, CuO, and .5 grams of powdered charcoal. Place the mixture in a hard glass test tube (ignition tube); clamp the tube in a nearly horizontal position and heat strongly. The test tube may be provided with a cork and delivery tube which should dip into a solution of calcium hydroxide, $Ca(OH)_2$, in a test tube, or this second test tube containing the $Ca(OH)_2$ solution may be held vertically under the mouth of the other tube so that the heavy gas which is evolved when the mixture is heated may fall into the tube, then close the tube with the thumb and shake. Explain the milky appearance of the solution. Examine the residue in the ignition tube. This may be done by rubbing it in the mortar and washing away the lighter particles. Results? Explain. Equation?

Recall the interaction of As_2O_3 and charcoal when heated together (?).

Equation? What is such a type of reaction called? Is carbon a chemically active substance at ordinary temperatures? How does the charring of wood preserve it?

Carbon and Oxygen.

Experiment II.—Preparation and Properties of Carbon Dioxide.

(*a*) Recall or repeat Exp. III. "Oxygen" (?). Do carbon and oxygen react at ordinary temperatures? What is formed by their interaction? Equation? What is the usual test for carbon dioxide?

(*b*) Show that CO_2 is formed when ordinary combustibles, such as wood, paper, illuminating gas, etc., are burned in air.

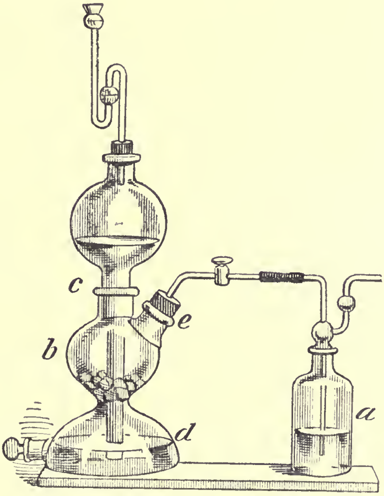


FIG. 40.—Kipp Generator.

(*c*) Hold a piece of charcoal in the Bunsen flame and describe its *combustion*. Products? Repeat experiment using *graphite* (pencil lead) (?). Define combustion.

(*d*) Pour a few cm.^{3} of clear limewater ($Ca(OH_2)$) into a test tube and by means of a glass tube blow air from the lungs through the liquid. Result? Explain. Would you infer that carbon undergoes combustion within the human body?

(*e*) Usual laboratory method of preparation (Fig. 40). Put several small pieces of marble (calcium carbonate, $CaCO_3$) in the hydrogen generator and add enough water to seal the bottom of the thistle tube. Connect the generator with a wash bottle half filled with strong sulphuric acid. Pour strong hydrochloric acid into the flask, as needed, through the thistle tube. Collect five or six bottles of the gas by displacement of air, placing the bottle with the mouth upward. Prove that the evolved gas is carbon dioxide. Note its color, odor and taste. Is the gas combustible? Does it support combustion? Pour one bottleful of the gas very slowly into another bottle of about the same size containing air. Lower a lighted splinter into the second bottle. Result? Conclusion? Is the gas heavier or lighter than air?

Counterpoise a beaker on the balance, then pour carbon dioxide into it (?).

Filter the contents of the generating flask; evaporate (hood) a portion of the filtrate to dryness; heat the residue until fumes of hydrochloric acid cease to be evolved. Dissolve a portion of the residue in distilled water and test for a chloride. Test for calcium by dipping a clean moist platinum wire into the solid residue and holding it in the Bunsen flame. A yellowish-red flame indicates the presence of calcium. What is the name of the salt (residue) in the evaporating dish? Indicate by equations the reactions involved in the preparation of carbon dioxide.

(*f*) Try the action of hydrochloric acid upon small portions of each of the following salts: sodium carbonate (Na_2CO_3), sodium hydrogen carbonate ($NaHCO_3$), potassium carbonate (K_2CO_3), barium carbonate ($BaCO_3$). Results? Is CO_2 evolved in each case? (Use the "loop tube" to carry a film of lime-water to the mouth of the test tube. This renders the testing for carbon dioxide a very simple process.)

(*g*) Place about a gram of sodium carbonate or powdered magnesite ($MgCO_3$) in a test tube, and heat strongly. Is carbon dioxide evolved?

Interpret the following equations:

$$\begin{aligned} \text{C (charcoal)} &+ O_2 \rightarrow CO_2 + 96{,}980 \text{ cal.} \\ \text{C (retort carbon)} &+ O_2 \rightarrow CO_2 + 96{,}530 \text{ cal.} \\ \text{C (graphite)} &+ O_2 \rightarrow CO_2 + 93{,}360 \text{ cal.} \\ \text{C (diamond)} &+ O_2 \rightarrow CO_2 + 93{,}240 \text{ cal.} \end{aligned}$$

Experiment III.—Optional. Synthesis of Carbon Dioxide.

This operation may be carried out by drawing simultaneously purified air through a tube over hot charcoal, and the product into a solution of calcium or barium hydroxide. (Instructions.)

Experiment IV.—Carbonic Acid. Carbonates.

(*a*) Half fill a clean bottle with distilled water; test the water with litmus paper or a few drops of a solution of phenolphthalein (?). Allow a stream of carbon dioxide to bubble through the water until the latter is saturated. Test the water with litmus paper. Results? Conclusions? Ascertain the relative conductivity of the solution (?). CO_2 is the anhydride of what acid? (This acid, carbonic (H_2CO_3), has never been prepared in the free state.) Is the acid stable? If not, into what substances does it decompose? What ions does the acid yield? Is it a "strong" acid? State the reasons for your answer.

Can you explain why carbonic acid is so readily liberated from carbonates? State Berthollet's law. Henry's law.

$$(CO_2, Aq.) = 5800 \text{ cal.}$$

(*b*) Conduct carbon dioxide into lime-water, or baryta water ($Ba(OH)_2$) until the gas ceases to be absorbed. Results? Filter and test the precipitate for carbon dioxide (?). What salt is formed by the action of CO_2 on lime-water? Is it soluble in water? In acids? Equations?

Saturate a solution of sodium hydroxide with carbon dioxide. Set the solution aside and allow the liquid to evaporate spontaneously. Prove that the residue is a *carbonate*. Equations?

What class of salts are yielded by carbonic acid ($H_2O + CO_2$)? What is the *basicity* of carbonic acid? How would you determine whether a rock specimen contained a carbonate or not?

Experiment V.—Formation of Calcium Acid Carbonate.

Conduct carbon dioxide into lime-water until the precipitate which forms at first, disappears. Filter. Divide the filtrate into two portions. To one portion add clear lime-water (?). Heat the second portion in a test tube (?). Why did the precipitate disappear in the first reaction? Why does it appear after heating? Equations? Explain the formation of the incrustations on the inside of tea-kettles and steam boilers.

All normal carbonates except those of the alkalies are insoluble in water. They are decomposed by hydrochloric acid with an evolution of carbon dioxide.

Experiment VI.—Optional. (Quant.) Estimation of Carbon Dioxide in a Carbonate.

(*a*) Report a method for the determination of carbon dioxide in a carbonate in which the evolved gas is absorbed in a weighed apparatus.

(*b*) Estimation by difference. The epitome of the process is as follows: A known weight of the carbonate is decomposed by dilute acid in a weighed apparatus and the carbon dioxide is dried as it escapes or is expelled through a bulb containing strong sulphuric acid. The loss in weight which results represents the carbon dioxide in the substance being examined.

Schrötter's apparatus is a convenient form of the apparatus required for the performance of this experiment. Draw a diagram of the apparatus and explain its manipulation. (See model in laboratory or text books on analytical chemistry. Figures of various forms of the apparatus usually appear in catalogues of laboratory supplies.)

Experiment VII.—(Quant.) Determination of the Density of Carbon Dioxide. Molecular Weight.

Provide a 300 $cm.^3$ flask with a tightly fitting rubber cork. See that the apparatus is perfectly clean and dry. Weigh the flask and cork.

Record this weight as the weight of flask, cork, and air which filled flask. Fill the flask with carbon dioxide by displacement of air; stopper the flask and weigh. Record weight. Repeat the operation of filling the flask with carbon dioxide and weighing, until the weight becomes practically constant. Calibrate the flask as in previous experiments. The weight of the empty flask is found by subtracting from the weight of the cork and flask filled with air the weight of a volume of air equal to the capacity of the flask. (Air under normal conditions, 1 $cm.^3$ = .00129 gram.) What is the weight of the carbon dioxide in the flask? Of 1 litre of the gas?

Calculate the molecular weight of carbon dioxide from the experimental data (?). What is your percentage of error?

Mention sources of error in determining the density of the gas by above method.

Experiment VIII.—Preparation and Properties of Carbon Monoxide.

(*a*) Assemble apparatus similar to that which you used for the preparation of chlorine. Put 10 grams of oxalic acid ($C_2H_2O_4$) in the generating flask. Half fill the wash bottle with lime-water or a caustic-soda solution. Pour 35 $cm.^3$ of concentrated sulphuric acid through the thistle tube into the flask; heat the latter gently. Collect three or four bottles of the evolved gas over water. Add a few drops of lime-water to a bottle of the gas; place your hand over the mouth of the bottle and shake vigorously. Is there any evidence that carbon dioxide is present? Set fire to a bottle of the gas and notice the characteristic blue flame. After the gas has burned, pour a few $cm.^3$ of lime-water into the bottle; shake. Results? Describe any visible changes that may have occurred in the wash-bottle. Add a few drops of acid to the solution and test for carbon dioxide (?). What gas besides carbon monoxide was evidently evolved by the action of H_2SO_4 on $C_2H_2O_4$? This chemical action is due largely to what particular property of sulphuric acid? Equations? May CO act as a reducing agent? Explain. Interpret the following equations (?).

(*b*) Optional. Intimately mix 2 grams of zinc oxide (ZnO) and 1 gram of powdered charcoal. Introduce the mixture into a hard glass test tube and heat strongly. Apply a flame to the mouth of the tube. Result? Equations?

$$(C, O) = 28{,}500 \text{ cal.} \qquad (CO,O) = 68{,}400 \text{ cal.}$$

$$Cu,O\ (37{,}100 \text{ cal}) + C,O\ (28{,}500 \text{ cal.}) \rightarrow Cu + C,O_2\ (96{,}900 \text{ cal.}) + 31{,}300 \text{ cal.}$$

"If an element combines with another according to multiple proportions, there usually occurs, in the union of the first atom, a greater disengagement of heat than with the following atom (compare nitrogen oxides). The numbers above, on the contrary, show that the union of the second atom of oxygen with carbon (CO,O) sets free 68,400 calories; that of the first atom (C,O), however, only 28,500 calories.

This can only be explained by the fact that, for the vaporization and disaggregation of the solid carbon molecules, heat is necessary. If we assume that the direct union of the first atom also disengaged 68,400 calories, it would follow from this that, in the dislocation of twelve parts carbon (amorphous) by weight into gaseous free atoms, 39,900 (68,400-28,500) calories were absorbed." Richter.

The above equations, indicating the heat disengagement for each stage in the oxidation of carbon, furnish an excellent illustration of the Law of Hess. (State the law.)

Experiment IX.—(Quant.) Determination of the Density of Carbon Monoxide. Molecular Weight.

The density of carbon monoxide may be determined by a method identical with that recorded in Exp. III. "Nitrogen and the Atmosphere."

Carbon and Hydrogen (Hydrocarbons).

Experiment X.—Preparation and Properties of Methane (Marsh Gas).

Heat a few grams of sodium acetate in a porcelain dish until the water of crystallization has been expelled. Heat a mixture consisting of equal parts of dehydrated sodium acetate and soda lime in a hard glass test tube clamped in a nearly horizontal position. The tube should be fitted with a cork and delivery tube. Collect the gas over water. Note its odor, color and taste. Does it burn? Does the gas explode when mixed with air? Attach a jet to the delivery tube and burn the gas when all the air has been displaced from the apparatus. Note the degree of luminosity of the flame. Is water formed during the burning of the gas? Test. Carbon dioxide? Test. Equations? What is the name and molecular formula of the gas?

$$(C,^* H_4) = 21,700 \text{ cal.} \qquad (C_2, H_6) = 28,600 \text{ cal.}$$

Experiment XI.—(Optional.) Preparation of Ethylene by Elimination of Water from Alcohol. Ethylene Bromide.

The following method is suggested by Gattermann: A mixture of 25 grams of alcohol and 150 grams of concentrated H_2SO_4 is heated, not too strongly, in a liter round flask on a wire gauze covered with thin asbestos, or sand bath. As soon as an active evolution of ethylene takes place, add, through a dropping funnel, a mixture of one part alcohol and two parts concentrated H_2SO_4 (made by pouring 300 grams of alcohol into 600 grams of sulphuric acid, with constant stirring), slowly, so that a regular stream of gas is evolved. If the mixture in the flask forms badly with a separation of carbon, it has been too strongly heated, and it is advisable to empty the flask and begin the operation anew. In order to free ethylene from alcohol, ether and sulphur dioxide, it is passed through a wash bottle containing sulphuric acid, and a second

* Amorphous carbon.

one, provided with three tubulures, the central one supplied with a safety-tube, containing a dilute solution of caustic soda. It is well to use a third wash bottle containing sulphuric acid. When the air in the apparatus has been displaced, fill a small narrow-mouthed bottle provided with a greased glass stopper, with the gas by downward displacement of air. Allow a drop of bromine to fall into the bottle, then replace the stopper quickly. Observe any changes taking place within the bottle After a few minutes remove the stopper under water. Results? Explain. Attach a jet to the delivery tube and burn the gas. Compare the degree of luminosity of the flame with that of methane (?). Equations?

$$(C_2, H_4) = \quad -2700 \text{ cal.}$$

Experiment XII.—Preparation and Properties of Acetylene.

Fit a test tube with a single-hole stopper carrying a piece of straight glass tubing about 5 cm. long and ending flush with the lower side of the stopper. Fill the test tube nearly full of water then drop into it a small piece of calcium carbide, CaC_2; insert the stopper. Note the odor of the evolved gas. When the air in the tube has been displaced, light the gas which is issuing from the jet. Describe the character of the flame. Hold a glass plate just above the flame (?). Would you infer that there is perfect combustion of carbon? Why? What is the name and molecular formula of the gas? Equations indicating the action of the *carbide* on water and the combustion of the gas? Will air burn in an atmosphere of the gas? Can you offer a possible explanation as to

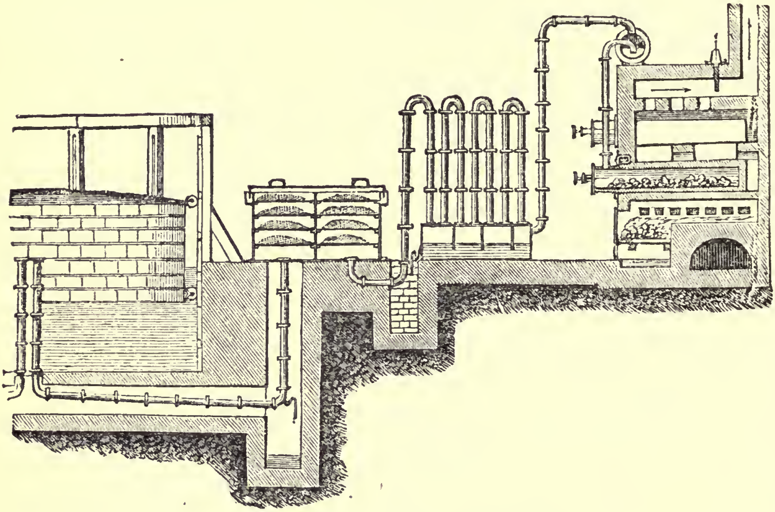


FIG. 41.—The Manufacture of Coal Gas.

why C_2H_2 and C_2H_4 are endothermic compounds, and CH_4 and C_2H_6 are exothermic? (See carbon monoxide.) $(C_2H_2) = -47{,}800$ cal.

Coal Gas is formed by the *destructive* distillation (Fig. 41) of bituminous coal. The composition of the products obtained depend largely upon the nature of the coal and the process of distillation. These products are: (1) *coke;* (2) *coal tar;* (3) *gas liquor* containing ammonia and other products, and known as *ammoniacal liquor;* and (4) *coal gas.* The coal gas is a mixture of various gases. The components of the mixture may be divided into three classes as follows:

Illuminants. (About 6%)	Diluents. (About 90%)	Impurities. (About 3%)
Ethylene, C_2H_4	Hydrogen, H_2	Nitrogen, N_2
Propylene, C_3H_6	Methane, CH_4	Carbon dioxide CO_2
Butylene C_4H_8	Carbon monoxide CO	Hydrogen sulphide, H_2S
Acetylene C_2H_2		Ammonia, NH_3
Allylene, C_3H_4		
Benzene, C_6H_6		
Heavy hydrocarbons.		

Some of the impurities are removed entirely from the purified gas; i.e., before the gas is delivered to the gas mains. The gas is often called "illuminating gas." The student is referred to Sadtler's Hand-book of Industrial Organic Chemistry and Thorpe's Outlines of Industrial Chemistry.

Experiment XIII.—Preparation and Properties of Illuminating Gas.

Fill a hard glass test tube one-half full of coarsely powdered bituminous or cannel coal; place a plug of glass wool or shredded asbestos above the coal to hold it in place; clamp the tube in a horizontal position and connect it with an empty wash bottle which communicates with a U-tube containing strips of litmus paper in one limb and filter paper moistened with lead acetate in the other limb; a third wash bottle is one-third full of lime-water. Heat the ignition tube gently with the Bunsen flame. As soon as all of the air has been driven out of the apparatus collect two bottles of the gas by water displacement. Disconnect the apparatus. Examine the gas in the bottles, noting its color, odor, inflammability and color of flame. Of what does the gas consist? Does the residue in the ignition tube suggest some form of carbon? What name is applied to it? Describe in full and explain any changes which may have occurred within the wash-bottles. What are the products of the combustion of the chief components of illuminating gas? Devise an experiment to prove your conclusions. (*Hint.*—Use gas from jet.)

Make a brief statement of the composition and manufacture of "producer gas." Of "water gas."

Carbon and Sulphur.

Experiment XIV.—Properties of Carbon Disulphide.

Procure a few $cm.^3$ of carbon disulphide in a test tube from the side-shelf reagent. Note its odor, color and high refractive index. What is its specific gravity? Place a drop of the liquid on the hand and force air over it (?). Place a very small quantity of the substance in an evaporating dish, then bring the heated end of a glass rod near the surface of the liquid (?). Would you infer that carbon disulphide is very inflammable? Is it miscible with water? With alcohol? It has been used in previous experiments as a solvent for what substances? Is rubber soluble in it? If so, allow the liquid to evaporate spontaneously. Result? Enumerate other uses of carbon disulphide. What is the molecular formula of carbon disulphide? Is it an endothermic compound? (See following equation.) What would you infer as to its stability?

$$(C, S_2\text{—liq.}) = -19{,}600 \text{ cal.}$$

Carbon and the Halogens.—Although carbon does not combine directly with the members of the halogen family, halides of carbon are formed by the action of the halogens on the *hydrocarbons*. (Recall Exp. XI.) In our previous work we have observed that chlorine is capable of withdrawing or *substituting* itself for the hydrogen of water, hydrogen sulphide, ammonia, etc. The halogens react very similarly with the hydrocarbons forming, by a process termed *substitution*, a series of carbon compounds known as *substitution products*. By such reactions the following familiar substances are obtained: Methyl-chloride (CH_3Cl), chloroform ($CHCl_3$), iodoform (CHI_3), carbon tetrachloride (CCl_4), etc. The latter (CCl_4) is a colorless liquid having a peculiar odor. It has a sp. gr. of 1.6 and boils at 77°. It is the final product of the action of chlorine upon methane (CH_4) or upon chloroform.

$$\begin{aligned} CH_4 + Cl_2 &\rightarrow CH_3Cl + HCl \\ CH_4 + 2Cl_2 &\rightarrow CH_2Cl_2 + 2HCl \\ CH_4 + 3Cl_2 &\rightarrow CH\,Cl_3 + 3HCl \\ CH_4 + 4Cl_2 &\rightarrow CCl_4 + 4HCl \end{aligned}$$

$$(C, Cl_4\text{ — gas}) = 21{,}000 \text{ cal.} \qquad (C, Cl_4\text{—liq.}) = 28{,}300 \text{ cal.}$$

$$(C_2, Cl_4\text{ — gas}) = -1100 \text{ cal.}$$

The *heats of formation* of the chlorides of carbon approximate those of the hydrogen derivatives, indicating that the affinity of the two elements for carbon is practically the same.

Carbon and Nitrogen.—These two elementary substances apparently do not possess any direct affinity for one another, therefore the union of the two is usually effected by indirect processes. However, small quantities of *cyanogen* (CN or Cy) are formed when electrical discharges take place between carbon poles in an atmosphere of nitrogen. The production is facilitated if one, at least, of the elements is in the form of a compound. Cyanogen is an endothermic compound—a colorless gas with an odor resembling that of peach blossoms, or better, almonds. It burns with a characteristic violet-blue flame, or more accurately, with a "pink flame edged with green." Its sp. gr. is 1.805 (Air = 1). Nascent cyanogen is recognized as a radical or group with the formula, CN. It is seen at once from its structure ($-C \equiv N$) that it is an unsaturated compound—a negative univalent radical. Like other univalent groups (OH, NH_2, CH_3), it cannot exist in the *free* state, but combines with itself to form a double molecule of *free cyanogen* (C_2N_2), known as dicyanogen. The structural formula ($N \equiv C - C \equiv N$) shows carbon satisfying its own bonds.

In its chemical relations carbon exhibits the mutability peculiar to organic groups. It combines with hydrogen under the influence of a quiet electric discharge to form the very "weak" but extremely poisonous *hydrocyanic* or *Prussic acid* (HCN). This acid is a colorless mobile liquid which boils at about 27°.

An aqueous solution possesses small electrical conductivity. It forms cyanides by exchanging its hydrogen for metals. These salts, with the exception of potassium cyanide which undergoes hydrolysis to a marked degree, are relatively stable and uniformly poisonous. The extreme feebleness of the acid is shown by the fact that the carbon dioxide of the air liberates it. For this reason the salt usually possesses the odor of hydrocyanic acid.

The tendency of the salts, like potassium cyanide (KCN), in the presence of easily reducible and highly heated oxides to form *cyanates* ($KCNO$) indicates that hydrocyanic acid is an unsaturated compound, and possesses a structure similar to that indicated by the following formula, $H - N = C =$. This behavior of potassium cyanide accounts for its frequent use as a suitable flux for securing reductions. It manifests a similar tendency to combine with sulphur, forming a salt belonging to a class known as the *thiocyanates*, e.g., $KCNS$.

Cyanogen also unites with iron to form a compound or rather a group which combines with various other metals to produce two series of salts, namely, the *ferrocyanides* and the *ferricyanides*. The potassium salt of the former, potassium ferrocyanide ($K_4Fe(CN)_6.3Aq.$), has been given the name of *yellow prussiate of potash;* the corresponding salt of the latter is known as potassium ferricyanide, $K_3Fe\,(CN)_6$ or K_6FeCy_6.

$$(C, N, H,\text{—gas}) = -27{,}500 \text{ cal.}$$

Experiment XV.—Preparation and Properties of Cyanogen.

Note.—This gas is intensely poisonous and should not be prepared by the student.

Cyanogen may be prepared by (1) heating the cyanides of mercury or silver; (2) the dry distillation of ammonium oxalate, and (3) the fusion of potassium cyanide and mercuric chloride.

$$Hg(CN)_2 \rightarrow Hg + \overline{C_2N_2}$$
$$(NH_4)_2C_2O_4 \rightarrow 4H_2O + \overline{C_2N_2}$$
$$2KCN + HgCl_2 \rightarrow Hg + 2KCl + \overline{C_2N_2}$$

Experiment XVI.—Preparation and Properties of Potassium Cyanide. Potassium Thiocyanate.

(*a*) Potassium cyanide (KCN) may be prepared by heating a nitrogenous carbon compound like gelatin ($C_{42}H_{66}N_{13}O_{16}$, approx.), with a small piece of potassium. The KCN which forms is extracted with water.

To a few cm.^{3} of a silver nitrate solution add a few drops of a solution of KCN. Results? Add an excess of KCN. Result? Equations?

(*b*) A test for cyanogen compounds. To a dilute aqueous solution of KCN add equal quantities of a ferrous and a ferric salt. Result? Add an excess of a potassium hydroxide solution, then acidify with HCl. Results? Before attempting to state the composition of the final product, add a few drops of potassium ferrocyanide ($K_4FeC_6N_6$) to a solution of a ferric salt. Result? What are your conclusions now as to the composition of the product referred to above?

(*c*) Potassium thiocyanate. Place two or three cm.^{3} of a KCN solution in an evaporating dish and add ammonium polysulphide $(NH_4)_2S_x$ until the color of the latter persists. Evaporate to dryness. Dissolve a portion of the residue in water; add a few drops of a ferric chloride ($FeCl_3$) solution (?). Test a solution of potassium thiocyanate (KCNS), shelf reagent, with a few drops of $FeCl_3$ (?). If the solution you prepared gave a black precipitate when $FeCl_3$ was added, heat the residue again in the evaporating dish and repeat test with $FeCl_3$. What is the name of the prepared substance? Its formula? Equations? What is the action of a solution of potassium thiocyanate upon solutions of ferrous salts?

Test the tap water for iron by evaporating 100 cm.^{3} to small bulk; add a few drops of HNO_3 (?) and heat to boiling. Cool the solution, and add a few drops of a KCNS solution (?).

All the single cyanides, except those of the alkalies, alkaline earths and mercury (ic) are insoluble in water. Barium cyanide is difficultly soluble.

Experiment XVII.—A Study of Flames.

(*a*) Recall or repeat the experiment with the Bunsen burner.—Preliminary Exercises.

(*b*) Light a Bunsen burner. Bring a cold piece of brass or iron wire gauze down upon the flame. Observe that the flame does not pass through the gauze (Fig. 42). Is this due to the absence of combustible gases? Apply a lighted match above the gauze (?). Why did the flame not pass through the gauze? Turn off the gas; hold a piece of gauze 3 or 4 cm. above the top of the burner; turn on the gas and hold a lighted match above the gauze (?). Explain results. Define "kindling temperature." What is the principle upon which the miner's safety lamp (Fig 43) is constructed?

(*c*) Open and close the holes of the lighted burner several times. Results? Hold a piece of glass tubing in the "luminous flame" of the burner (?). Open the holes at the bottom of the burner and hold the blackened rod in the non-luminous flame (?). Account for the deposition of carbon and its disappearance. What is the probable cause of the luminosity of the flame? Test your conclusion as follows: Place a small quantity of powdered charcoal in a piece of glass tubing and blow the particles of carbon into one of the holes at the base of the burner. What is the effect on the luminosity of the flame? Explain. Why do a number of the "burning oils" burn with a "sooty" flame? Why is the hydrogen flame non-luminous? What is the source of the powerful light emitted by a Welsbach burner? What is the object of the holes at the base of the burner? Why is the Bunsen flame non-luminous? Why does the gas ordinarily burn at the top of the tube and not on the inside? What causes the flame to "strike back" occasionally and burn inside the tube?

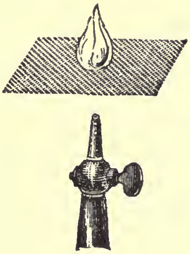


FIG. 42.

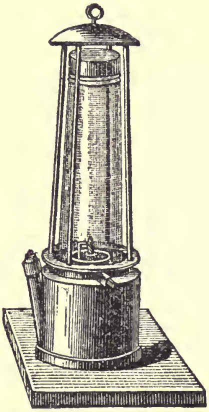


FIG. 43.—Davy's Safety Lamp.

(*d*) Slightly bend a glass tube about 15 cm. long; introduce the shorter arm in the flame about 2 cm. above the top of the burner. Light the gas issuing from the tube. What are your conclusions concerning the conditions existing in this portion of the flame? Explain.

(*e*) Oxidizing and reducing flames. Examine and sketch the parts of a very small luminous flame.

Hold a piece of bright copper wire horizontally across a Bunsen flame so that the wire cuts the inner cone. Observe that the portion of the wire in the inner cone remains bright, while those portions in contact with the edges of the flame become coated with a dark substance (copper oxide, CuO). The copper has undergone what kind of a chemical change? Move the wire so as to bring the *oxidized* portion into the inner cone, the metal becomes bright owing to a *reduction* of the oxide. The outer cone of the flame where oxygen is in excess is called the *oxidizing* flame; the inner cone, in which heated and unburnt combustible gases exist (hydrogen and hydrocarbons), is referred to as the *reducing* flame. Both cones exist in all ordinary flames.

FIG. 44.

(*f*) Use of the blow-pipe. Ask the instructor how to produce the oxidizing and reducing flames by means of a blow-pipe. Ascertain the effect of each flame by heating an intimate mixture of lead oxide (PbO) and sodium carbonate on charcoal in the reducing cone, and a small piece of metallic lead on charcoal in the oxidizing cone. Results?

(*g*) Examine and sketch a candle flame (Fig. 44). Is there any essential difference between a gas flame and a candle flame or a lamp flame? All flames are the result of the interaction of what state of matter? Define "a flame."

(*h*) Examine a lamp burner. Does its structure embody principles analogous to those of the Bunsen burner? Explain. Why are some lamps provided with a "central draft?" Can you explain the cone-like shape of the flame of the Bunsen burner?

The following table gives the results of a series of accurate experiments conducted for the purpose of determining the actual temperatures of various regions of the Bunsen flame. The cooling effect of the diluent, air, is observed in portions of the non-luminous flame.

TEMPERATURE OF FLAME OF BUNSEN BURNER.

(Data for a burner burning six cubic feet of coal gas per hour.)

(Lewes–Newth.)

Region in Flame.	Luminous.	Non-luminous.
One-half inch above burner	135°	54°
One and one-half inch above burner	421°	175°
Tip of inner cone	913°	1090°
Center of outer cone	1328°	1533°
Tip of outer cone	728°	1175°
Side of outer cone, level with tip of inner cone	1236°	1333°

SILICON, Si.

At. Wt. 28.4 Mol. Wt. (?).

It has been estimated that 27.3 per cent. of the earth consists of **silicon.** However, owing to its great affinity for oxygen, it does not occur in nature as an uncombined element. In the combined condition it most frequently occurs as silicon dioxide (silica, SiO_2) and in the form of salts of silicic acid—silicates. Silicon, like carbon, occurs in several forms, of which *amorphous* and *crystalline* forms are accurately known. Amorphous silicon is a non-lustrous greenish-brown powder which when set on fire in the air undergoes incomplete combustion owing to the formation of an incombustible layer of silicon dioxide.

Crystalline silicon (sp. gr., 2.49) is a grayish-black octohedral crystal possessing a metallic luster. It does not change appreciably in the air even at red heat. It is soluble in hot caustic soda. (Molten iron or zinc dissolves silicon; when they cool, the silicon separates in crystals.)

The most important compound of silicon is silicon dioxide, the anhydride of silicic acid. It occurs in several varieties—two crystalline and one amorphous. It is most widely distributed in the crystalline form as *quartz* or rock crystal. There are several colored varieties of quartz, the color being due to the presence of impurities. Quartz has a density of 2.66 and stands seventh in the scale of hardness. (See Appendix.) The other crystalline form of silicon dioxide is known as *tridymite*. It occurs almost solely in the form of microscopic crystals as a constituent of various rocks. The sp. gr. of tridymite is 2.3. *Amorphous* silicon dioxide (sp. gr., 2.2) occurs most abundantly in the form commonly known as *flint*. The opal represents another impure form. Jasper, chalcedony, etc., are "crypto-crystalline," i.e., are composed of small crystals. Silica dissolves in the fused hydroxides and carbonates of the alkalies, but is insoluble in water and all acids except hydrofluoric acid. At the high temperature of the oxyhydrogen flame silicon dioxide melts forming a viscous glass-like fluid which can be blown into any desired shape. On account of its high melting-point and resistance to chemical action, this amorphous "quartz-glass" has been used extensively in recent years for making vessels for use in chemical laboratories. It has a very small coefficient of expansion with heat and can, therefore, be subjected to sudden changes of temperature without cracking.

In its *chemical relations* silicon bears a close resemblance to carbon. It is essentially non-metallic in these relations. The natural silicates form a numerous and complex class of minerals which may be regarded as compounds of metallic oxides with silicon dioxide; as *feldspar*, Al_2O_3,-K_2O, $6SiO_2$.

Experiment I.—Preparation and Properties of Silicon.

(*a*) Procure a piece of crystalline silicon from the instructor. Examine it carefully. Tabulate its observed properties. What is its sp. gr.? Enumerate the several forms in which silicon occurs.

(*b*) Thoroughly mix in a mortar 1 gram of magnesium powder and 2 or 3 grams of *powdered* quartz sand. Place the mixture in a wide hard glass tube; heat the tube to bright redness in the flame of a blast-lamp, slowly rotating the tube. After a few minutes' heating, dissolve out the soluble portions of the fused mass with water and HCl. The residue consists of *amorphous silicon* and quartz sand.

(*c*) Ascertain the action of the following reagents upon silicon and tabulate results: HCl, H_2SO_4, HNO_3, and a KOH solution.

Experiment II.—Silicon Dioxide. Silicates. Silicic Acid. Hydrogele.

(*a*) Examine specimens of quartz, sand, agate, opal, amethyst, onyx, flint, infusorial or diatomaceous earth, etc. Make a list of those examined.

(*b*) Test the solubility of silicon dioxide in the various acids and alkalies. Tabulate results. Recall the action of H_2F_2 on silica (SiO_2). See Exp. III, "Fluorine." Equation?

(*c*) To 2 cm.^{3} of a solution of sodium silicate (water glass, Na_2SiO_3) in an evaporating dish or casserole, add 15 or 20 cm.^{3} of water, then add concentrated HCl until the solution is strongly acid. Note the formation of a white gelatinous precipitate. What is it? Formula? Equation? *Note.*—These jelly-like precipitates are sometimes termed "*hydrogeles.*"

Evaporate the solution to dryness on a sand or steam bath. Now heat the dish with the flame. When the dish has cooled, treat the residue with water; filter. Remove the residue from the filter paper and heat it in a covered crucible supported by a pipe-stem triangle. Results? What is the substance in the crucible? Its formula? Rub some of it between the fingers. Do you detect any grit? Is it crystalline or amorphous?

Silic acid (probably H_4SiO_4) shows a tendency to form "colloidal solutions" or "pseudo-solutions." When hydrochloric acid is added to a concentrated solution of a soluble silicate, the silicic acid separates out as a gelatinous mass, but if a dilute solution of the silicate is substituted and an excess of the acid used, precipitation does not take place and the solution remains clear and apparently unchanged. It appears as if the silicic acid were difficultly soluble in water, but dissolved when much water was used. It has been found, however, that this is not the case. The silicic acid is present (suspended) in the water in the *colloidal* state. The apparent solution of silicic acid is not a true solution, but a "pseudo-solution." (A solution of this kind is sometimes termed a *hydrosole.*) This may be proven by subjecting the pseudo-solution to *dialysis*, when the salt (crystalloid) formed by the interaction of the metal and acid will diffuse freely through the membrane of a dialyser, while the silicic acid will be retained, as is in accord with the conduct of colloidal substances. Again, it is possible to partially precipitate the silicic acid from these "pseudo-solutions" by the addition of various substances, such as salts. Silic acid occurs very frequently in this form in nature as the result of the decomposition of certain silicates by carbonic acid. The various colored varieties of quartz were probably formed from silicic acid in this condition. This view is supported by the fact that it is now known that silicic acid, under suitable conditions, will crystallize out from such solutions.

(*b*) Fuse a mixture of 1 grm. of finely powdered feldspar with 4 or 5 grams of sodium carbonate* in a covered porcelain or platinum crucible.

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* A mixture of K_2CO_3 and Na_2CO_3 may be used as a flux. It is frequently expedient to use a fusion mixture consisting of 1 part of NH_4Cl and 8 parts of $CaCO_3$ by weight.

The crucible should not be more than half-filled. Heat gently until the frothing has ceased, then heat with the blast-lamp flame until the decomposition is complete and the contents of the crucible are in quiet fusion. When the crucible is cold it is placed upon its side in a beaker containing sufficient water to cover the crucible. Hydrochloric acid is now added until effervescence ceases, and no further precipitation of gelatinous silicic acid takes place. Filter. Transfer the *hydrogele* of silicic acid from the filter paper to a crucible and dehydrate it. Results? What is the substance which remains in the crucible after heating? Rub some of it between the fingers. Do you detect any grit? Equations?

Experiment IV.—Fluosilicic Acid. Fluosilicates.

(*a*) To 5 cm.³ of a solution of fluosilicic acid (H_2SiF_6) add a small quantity of a solution of potassium nitrate (KNO_3). Examine the precipitate of potassium fluosilicate.

(*b*) Prove that fluosilicates are decomposed when heated with H_2SO_4, and that silicon tetrafluoride is evolved. Recall Exp. III—"Fluorine." Record procedure. Equations?

(*c*) Repeat (*a*), using a solution of a sodium salt. Results? Equations?

(*d*) Repeat (*a*), using a solution of barium chloride. Results? Equations?

(*e*) Record the names and formulæ of the well-defined hydrides, halides and acids of silicon. What is *carborundum*? Its formula?

Experiment V.—A Test for Silicates. Silicon Tetraflouride.

(Hood.) Place 2 or 3 cm.³ of concentrated H_2SO_4 in a platinum crucible and add a small quantity of powdered silicate or substance to be tested. Warm the contents of the crucible gently; allow crucible to stand until effervescence ceases. When the contents of the crucible have cooled (Caution!), add 1 cm.³ of H_2F_2. Place the cover on the crucible in such a manner as to leave a small opening on one side. Hold a platinum loop containing a drop of distilled water at this opening; warm the crucible gently and observe whether white particles of silicic acid appear in the drop of water. Evaporate the drop to dryness on the crucible cover or a piece of platinum foil. A white residue which is not volatilized at a high temperature, proves that silica was present in the original substance. Equations?

All silicates save those of the alkali metals are insoluble in water. They are decomposed by hydrofluoric acid with the formation of silicon tetrafluoride. A very few of the insoluble silicates are decomposed by acids other than hydrofluoric. The insoluble silicates are usually converted into a soluble form by fusion with the carbonates of the alkalies.

The physical and chemical relations of carbon and silicon may be seen in the following table:

Physical Properties.	Carbon.	Silicon.
Atomic weight,	12.0	28.4
State or phase,	Solid (amorphous, crystalline)	Solid (amorphous, crystalline)
Color,	Black (amorph.) Black-gray (graph.)	Greenish-brown (amorph.) Grayish-black (cryst.)
Specific gravity,	2.2–3.5 (cryst.) (graphite, diamond)	2.4 (crystalline)
Specific heat,	<————————	————————<
Melting-point,	3500°?	1200°?
Chemical Properties.		
H-derivatives,	CH_4; C_2H_4, etc.	SiH_4
Heat of formation,	C, H_4=21,800 cal.	SiH_4=24,800 cal.
State or phase,	Gas	Gas
Halides	CCl_4; etc.	$SiCl_4$;
Heat of formation,	C,Cl_4=21,000 cal.	Si,Cl_4=157,000 cal.
State or phase,	Liquid	Liquid
O-derivatives,	CO; CO_2	SiO_2
Heat of formation,	C,O_2=96,980 cal.	Si,O_2=219,000 cal.
State or phase,	Gas	Solid
S-derivatives,	CS_2	SiS_2
Heat of formation,	C, S_2= —26,100 cal.	Si,S_2=40,400 cal.
State or phase,	Liquid	Solid.

PROBLEMS.

1. Five grams of pure graphite are completely burned in oxygen. What volume of carbon dioxide is formed? What is the heat of the reaction?

2. What volume of oxygen is necessary to burn 12 grams of carbon?

3. How many grams of pure calcium carbonate will be required to produce 10 liters of carbon dioxide?

4. What volume of carbon monoxide will be liberated by the action of H_2SO_4 on 10 grams of oxalic acid?

5. An analysis of the air in a lecture-room showed that 8.5 volumes of carbon dioxide were present in 10,000 volumes of air. If the room is 20 meters long, 17 meters wide and 7 meters high, what is the weight and volume of the carbon dioxide in the room?

6. Dumas and Stas found that 30 parts of carbon by weight combined with 80 parts of oxygen, and that the carbon dioxide formed contained its own volume of oxygen. A liter of carbon dioxide weighs 1.976 grams. From the foregoing data calculate the molecular weight and deduce the simplest formula of carbon dioxide. Deduce the atomic weight of carbon.

7. How many liters of carbon dioxide must be passed over red-hot

charcoal to yield 100 liters of carbon monoxide? To yield 25 grams of carbon monoxide?

8. A precipitate which when dry weighed 1.5 grams was formed by passing carbon dioxide through lime-water. What is the weight of the absorbed gas?

9. Calculate the precentage weight of CO_2 in calcium carbonate, sodium bicarbonate, and magnesium carbonate.

10. How many grams of oxygen will be required for the complete combustion of 5 grams of methane? Of 5 grams of ethylene? Of 5 grams of acetylene?

11. Calculate the percentage composition of marsh gas, ethylene and acetylene.

12. Water gas is prepared by passing steam over red-hot coal. The simplest equation for the reaction is:

$$C + H_2O \rightarrow \overline{H_2} + \overline{CO}.$$

What volume of water gas at 15° C. and 730 mm. will be formed from 50 grams of steam?

13. Scheele found that 0.6738 of silicon tetrachloride reacted with $AgNO_3$ to yield 2.2769 grams of silver chloride. Calculate the atomic weight of silicon.

14. Calculate the percentage composition of

Garnet,	$Ca_3Fe_2^{\cdot\cdot\cdot}(SiO_4)_3$
Mica,	$KH_2Al_3(SiO_4)_3$
Kaolin,	$H_2Al_2(SiO_4)_3, H_2O$
Serpentine,	$Mg_3Si_2O_7, 2H_2O$
Orthoclase	(feldspar), $KAlSi_3O_8$.

CHAPTER XXI.

SOME COMMON CARBON COMPOUNDS.

The simplest compounds of **carbon** are those which contain only hydrogen and carbon, e.g., CH_4, C_6H_6, C_2H_4. These compounds have been termed *hydrocarbons* and are regarded as the fundamental compounds of organic chemistry. Nearly all organic compounds are either hydrocarbons or hydrocarbon derivatives. Speaking comparatively, very few carbon compounds are known which do not contain hydrogen.

Although hundreds of hydrocarbons are known and an almost infinite number are theoretically possible, they may be arranged in a small number of comparatively simple series. These series correspond somewhat to the different groups of elements. Further, the members of one and the same series resemble one another much more closely than do the elements of a given series of the elements. In general, the members of any series bear such a close resemblance to one another, that if we understand the simpler members, we are able to anticipate many of the properties of the more complicated members. Attention is also directed to the fact that for each hydrocarbon in a series there is a corresponding class of derivatives and that the relations existing between any hydrocarbon and its derivatives are very similar to those existing between any other hydrocarbon of the series and its derivatives. It is obvious, then, that if we know the derivatives which can be yielded by a single hydrocarbon of a series, then we are able to prophesy with some degree of certainty the existence of the derivatives of every other hydrocarbon of the series.

The following table shows the classification of a number of the hydrocarbons as regards their empirical formulæ in three of the best known "series." It will be observed that each hydrocarbon differs from the one which precedes it by an atom of carbon and two of hydrogen. Such a series is known as an *homologous series* and may be represented by one general formula, $C_n\ H_{2n+2}$.

Methane Series. C_nH_{2n+2}		Ethylene Series. C_nH_{2n}		Benzene Series. C_nH_{2n-6}.	
Methane	$C\ H_4$	Ethylene	C_2H_4	Benzene	C_6H_6
Ethane	C_2H_6	Propylene . . .	C_3H_6	Toluene	C_7H_8
Propane	C_3H_8	Butylene	C_4H_8	Xylene	C_8H_{10}
Butane	C_4H_{10}	Amylene	C_5H_{10}	Mesitylene . .	C_9H_{12}
Pentane	C_5H_{12}	Hexylene	C_6H_{12}	Pseudocumene	C_9H_{12}
Hexane	C_6H_{14}	Heptylene . . .	C_7H_{14}	Durene	$C_{10}H_{14}$
Etc.				Cymene	$C_{10}H_{14}$

Saturation.—The hydrocarbons are frequently referred to as being *saturated* or *unsaturated* accordingly as they behave towards chemcal agents. Thus, if all the four valences of carbon are employed, the hydrocarbon having then no power to combine directly with other compounds or elements, it is said to be *saturated.*

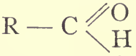
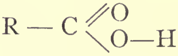
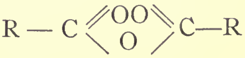
$$\mathrm{CH_4 + Cl_2 \rightarrow CH_3Cl + HCl.}$$

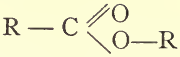
It is obvious that in the reaction indicated above chlorine must first displace hydrogen before it can enter into combination with the compound. On the other hand, if the hydrocarbon (any compound) can unite directly with elements or compounds it is spoken of as being *unsaturated;* for example, ethylene combines directly with chlorine to form ethylene chloride—

$$\mathrm{C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2.}$$

Organic Radicals.—The hydrocarbons may be regarded as *hydrides* of various *radicals,* as methyl hydride or methane, $\mathrm{CH_3.H}$, ethyl hydride or ethane, $\mathrm{C_2H_5.H}$, etc. As a matter of fact, hydrocarbons from which hydrogen has been removed give rise to *hydrocarbon radicals,* thus, $\mathrm{CH_3}$ is the organic radical *methyl* from methane, and $\mathrm{C_2H_5}$ is the radical *ethyl* from ethane. These groups of units, radicals, which are found to pass unaltered from compound to compound are like all other radicals, incapable of existing in the *free* state. Since in chemical reactions these organic radicals behave toward other elements and radicals in a manner similar to that in which the *metals* behave toward the nonmetals they are frequently termed positive radicals. They usually differ from the inorganic radicals in that they lack the property of forming ions. In general, organic substances may be most conveniently regarded as derived from these hyrdocarbon radicals, which in most cases are hydrocarbons possessing unsatisfied bonds of valency.

The following scheme, containing a partial list of the more important fundamental forms of the hydrocarbon derivatives may be of service in emphasizing the thought of the foregoing paragraph:

Hydrocarbons	$\mathrm{R-H}$
Alcohols	$\mathrm{R-O-H}$
Phenols	$\mathrm{R-O-H}$
Ethers	$\mathrm{R-O-R}$
Aldehydes	 $\mathrm{R-C\begin{smallmatrix}/\!\!/O\\ \diagdown H\end{smallmatrix}}$
Acids	 $\mathrm{R-C\begin{smallmatrix}/\!\!/O\\ \diagdown O-H\end{smallmatrix}}$
Ketones	$\mathrm{R-C-R}$
Acid anhydrides	 $\mathrm{R-C\begin{smallmatrix}/\!\!/O\ \ O\diagdown\!\!\diagdown\\ \diagdown\ O\ \diagup\end{smallmatrix}C-R}$
Halides	RCl, RBr, etc.

Esters	 $R - C \genfrac{}{}{0pt}{}{/\!\!/ O}{\diagdown O-R}$
Amides	 $R - C \genfrac{}{}{0pt}{}{/\!\!/ O}{\diagdown NH_2}$
Amines	RNH_2, R_2NH, etc.
Organo-Mineral Compounds	$R - M$
Carbohydrates	$C_6H_{10}O_5$, $C_{12}H_{22}O_{11}$, etc.

*Explanatory Note.**

Alcohols.—Composed of carbon, hydrogen and oxygen and containing one or more *hydroxyl* groups (OH), as *methyl-alcohol*, CH_3OH, *ethyl-alcohol*, C_2H_5OH.

Phenols.—Similar to alcohols in composition, but resembling the acids in many of their properties; however, they do not yield aldehydes when partially oxidized as *phenol*, $C_6H_5.OH$.

Ethers.—The oxides of the radicals; formed from the alcohols by the substitution of a hydrocarbon radical for the H in the hydroxyl, as *methyl-ether*, $CH_3.O.CH_3$; *ethyl-ether*, $C_2H_5.O.C_2H_5$.

Aldehydes.—Dehydrogenated alcohols; products of the partial oxidation of the alcohols, containing the group (COH), as *formaldehyde*, CH_2O; as *ethyl-aldehyde* (acet-aldehyde) $CH_3.COH$.

Acids.—Products of the further oxidation of the alcohols, containing one or more *carboxyl* radicals, CO_2H; as *formic acid*, CH_2O_2; *acetic acid*, CH_3 CO_2H or $CH_3.CO.OH$.

Ketones.—(Acetone, the simplest of the ketones, is prepared by the distillation of calcium acetate.) Formed from the acids by the substitution of a hydrocarbon radical for the OH in the carboxyl; contain the group CO, as acetic tetone or acetone $CH_3.CO.CH_3$.

Halides.—Formed from the foregoing groups by the substitution of a halogen radical for hydrogen or hydroxyl; as *chloroform*, $CHCl_3$; *iodoform*, CHI_3, *ethyl chloride*, C_2H_5Cl; *acetyl chloride*, $CH_3.CO.Cl$.

Esters (ethereal salts).—Formed from the acids by the substitution of a hydrocarbon radical for the hydrogen in the carboxyl radical; as *ethyl acetate*, $CH_3.CO.O.C_2H_5$.

Ammonia—Derivatives.—Formed upon the model of ammonia, NH_3, by the substitution of a radical for hydrogen; as *acetamide*, $NH_2.C_2H_3O$; *ethylamine*, $NH_2.C_2H_5$.

Organo-Mineral Compounds.—Formed upon the type of the chlorides of metals or non-metals by the substitution of hydrocarbon radicals for the chlorine, as *zinc ethide*, $Zn(C_2H_5)_2$.

Compounds for which the exact structure has not been fully established. They are classified according to similarity of properties, ultimate composition or products of decomposition.

Carbohydrates, or compounds usually containing six, or some multiple of six, atoms of carbon, together with some multiple of the group H_2O,† as *starch*, $C_6H_{10}O_5$; *glucose*, $C_6H_{12}O_6$; *sugar*, $C_{12}H_{22}O_{11}$.

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* Data from Bloxam.

† Rhamose ($C_6H_{12}O_5$) is an exception.

Glucosides, or compounds which yield glucose as one of their products of decomposition, as *salicin*, $C_{13}H_{18}O_7$.

Albuminoids and **Gelatinoids,** or compounds containing C, H, N and O, often with small quantities of S, and sometimes of P, distinguished by their tendency to putrefy when moist; *albumin*, *fibrin* and *casein* are examples of such compounds, but they cannot at present be represented by satisfactory formulæ.

Isomerism.—One of the most interesting facts with which we early become acquainted in the study of organic chemistry is the existence of entirely *different* compounds having the same *percentage* composition. Such compounds are called *isomeric* or briefly *isomers*. Isomers are of two kinds: (1) If the isomers have the same molecular weight they are known as *metamers*, as ethyl alcohol (C_2H_5OH) and methyl-oxide ($(CH_3)_2O$). (2) If they have different molecular weights, as acetylene (C_2H_2), benzene (C_6H_6) and styrene (C_8H_8), they are called *polymers*.

Isomers usually differ in both their physical and chemical properties. For example, the *empirical* formula C_2H_6O represents two substances (metamers)—the one a gas (methyl-oxide), the other a liquid (ethyl hydroxide or alcohol). Isomeric compounds undoubtedly owe their differences to different groupings or arrangements of the atoms within the molecules. It frequently occurs that one of the metamers can be made directly from the other. This gave rise to that variety of chemical change previously named "internal rearrangement."* In 1828, Wöhler effected the synthesis of a well-defined organic compound, urea, $CO(NH_2)_2$, from wholly inorganic materials. This was the first synthesis by a chemist, of a typical organic compound from a substance whose preparation is independent of life processes. Wöhler warmed a solution of ammonium cyanate, $NH_4.CNO$, which is a metamer of urea, for some time. On cooling the liquid, long prisms of urea were deposited.

$$NH_4CNO \rightleftarrows CO(NH_2)_2.$$

These two compounds are entirely different as regards their chemical properties. Ammonium cyanate is an ionizable *salt* while the latter (urea) is *not* a salt, but unites with acids like ammonia to form salts. The ammonium cyanate undoubtedly underwent an intramolecular change as indicated by above formulæ; at least the attempt is made to explain the difference in properties of the metamers by postulating a difference in the *molecular structure* or *constitution of the substances*.

It is quite probable that a difference in structure is closely related to a difference in energy-content of metamers. For example, fumaric and maleïc acids have the same *empirical* formula, $C_4H_4O_4$, but the "heat of combustion" of the former is 1338 Kj., while that of maleïc acid is 1365 Kj. This indicates that the energy-content of maleïc acid is greater than that of fumaric acid. The conclusion seems justified

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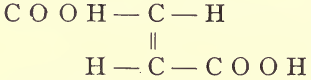
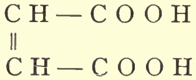
* One author suggests that there may be discovered 802 compounds of the ormula, $C_{13}H_{28}$.

when it is recalled that maleïc acid is the less stable of the two compounds and melts at 130°, while fumaric acid melts at a temperature above 200°. The following *structural* formulæ indicate a difference in the *constitution* of the two compounds:



$$\begin{array}{rcl} COOH-{} & C & -H \\ & \| & \\ H-{} & C & -COOH \end{array}$$

Fumaric acid
$(C_4H_4O_4)$



$$\begin{array}{l} CH-COOH \\ \| \\ CH-COOH \end{array}$$

Maleïc acid
$(C_4H_4O_4)$

Graphic or *structural* formulæ are the result of an endeavor to provide a "picture" of the way in which the atoms or radicals of a molecule are *linked* together.

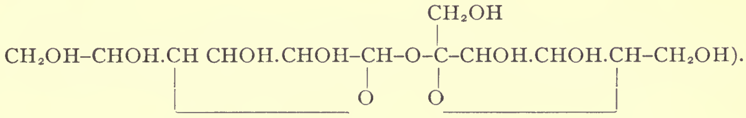
It is acknowledged that any success which has been or may be achieved in the synthesis of organic compounds has been or will be the result of the study of the *structure* of compounds.

The proving of the constitution of a substance represents in many cases one of the most difficult problems of organic chemistry. It usually involves an accurate and extended consideration of the reactions of the substance under consideration. In order that the student of inorganic chemistry may have some conception of the mode of procedure of a chemist endeavoring to prove the constitution of a substance, the following method is cited, and may be regarded as typical although it represents one of the simpler cases.

Determination of the Constitution of Alcohol.—(*a*) When alcohol reacts with hydrochloric acid, and the mixture is distilled at a low temperature, the products are water and a volatile liquid known as ethyl chloride, C_2H_5Cl. The interaction may be indicated by the equation, $C_2H_5OH + HCl \rightarrow C_2H_5Cl + HOH$. It is evident that the Cl of HCl has exchanged positions with the OH of the alcohol; this leads to the conclusion that alcohol is composed of at least two groups, namely the ethyl radical and the hydroxyl radical, and that its *rational* formula is $C_2H_5 . OH$.

(*b*) Again, sodium dissolves in alcohol (C_2H_5OH) with an evolution of hydrogen, forming a crystalline substance known as sodium ethoxide, C_2H_5ONa. It is seen that Na has displaced one atom of H. It might be supposed if an excess of Na were used, that the remaining H_5 might be displaced and a compound of the composition of C_2Na_6O, would be produced ultimately, but this is contrary to all experimental evidence. Na can be substituted for only one of the six atoms of hydrogen in alcohol. It is inferred then that one of the six atoms is "linked" or "fitted" into the intramolecular structure in a manner different from the other five. The concept is indicated by writing the formula for alcohol as follows, C_2H_5OH.

Chemists have been unable as yet to agree on the rational formula of many compounds, especially the carbohydrates, glucosides, alkaloids, etc. The following structural formula for cane-sugar ($C_{12}H_{22}O_{11}$) has been proposed:



$$\mathrm{CH_2OH{-}CHOH.\underset{|}{CH}\ CHOH.CHOH{-}\underset{\underset{O}{|}}{CH}{-}O{-}\overset{\overset{CH_2OH}{|}}{\underset{\underset{O}{|}}{C}}{-}CHOH.CHOH.\underset{|}{CH}{-}CH_2OH).}$$

Experiment I.—Hydrocarbons.

(*a*) Recall or repeat the experiments in which methane, ethylene and acetylene were prepared. Are these hydrocarbons gases, liquids or solids? Write the equations for the combustion of these three compounds.

(*b*) Examine small quantities of each of the following hydrocarbons and give the formula (of the main components if a mixture) for each. Classify them as to *state:* Gasoline, toluol, kerosene, naptha, benzine, petroleum, paraffine, benzene, ozokerite, vaseline and gasoline.

Experiment II.—(L. T.) Determination of the "Flashing-point" of Kerosene.

Note.—"The temperature at which oil gives off sufficient vapor to form a momentary flash when a small flame is brought near its surface" is known as the "*flash-point.*" The temperature at which oil gives off enough vapor to maintain a continuous flame if ignited, is ascertained by the "*fire test.*" The "*burning-point*" is about 10° C. higher than the "flash-point." The safety of kerosene depends largely on the absence of volatile hydrocarbons which may escape in sufficient quantities to form an explosive mixture with air. The presence of these hydrocarbons is determined by the *flashing test.*

(*a*) The simplest form of apparatus used for determining the flash-point consists essentially of a small beaker in which is suspended a thermometer. A small quantity of the kerosene to be tested is placed in the beaker and warmed slowly till a flame which is brought near to the surface at regular intervals of time, causes a momentary flash. At the flashing-point the vapor ignites, and the bluish flame runs down to the surface of the oil.

(*b*) A simple, but more accurate form of apparatus for determining the flashing-point may be prepared as follows: A rubber stopper provided with single perforation is fitted to one end of a piece of a glass cylinder 2.5 cm. in diameter, and 15 cm. long. One end of a piece of ordinary glass tubing about 40 cm. long is forced through the cork until it projects about 1 cm. beyond the inner surface of the cork; the tubing is then bent off, close to the cork, twice at right angles in such a manner that the long end of the tube is parallel and close to the cylinder; the tubing is finally bent on a level with the open end of the cylinder at right angles and away from the latter. The apparatus if made according to directions, has much the appearance of the old-fashioned, long-stemmed pipes. The bent tube contracts to a small orifice within the cork. Air is forced through this tube. The oil to be tested is poured into the cylinder until the latter is filled to a point such that when air is being forced through the apparatus, the surface of the foam is about 5 cm. from the top of the cylinder. The apparatus is now placed in a beaker of water—the surface of the oil and the water should be at the same level. Suspend a thermometer in the oil. Heat the contents of the beaker gently and force a slow current of air through the oil. Bring a small flame to the mouth of the cylinder for an instant as the temperature of the kerosene rises slowly, degree by degree. The lowest temperature at which the vapor ignites, as indicated by the bluish flame running down to the surface of the oil, is the flash-point.

Determine the flashing-points of two or three *grades* of kerosene.

From what you know of the properties of gasoline, would you infer that its flash-point is higher or lower than that of kerosene?

Experiment III.—Fermentation. Properties and Preparation of Alcohol.

(*a*) Dissolve 50 grams of grape sugar ($C_6H_{12}O_6$)* in 350 cm.³ of water, and add one-half of a compressed yeast cake. Place the mixture in a large flask (Fig. 45) or bottle provided with a one-hole rubber stopper; connect the flask with a wash bottle half filled with lime-water. The delivery tube of the wash bottle should be connected in series with a U-tube filled with caustic potash or soda-lime, the object of which is to prevent carbon dioxide in the air from acting upon the lime-water. Set the apparatus aside in a moderately warm place. Fermentation usually begins at once as is evidenced by the bubbling of carbon dioxide, one of

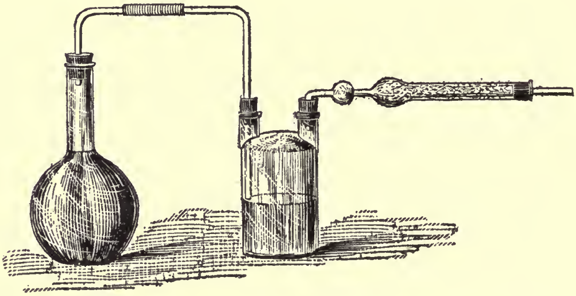


FIG. 45.

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* Cane sugar (ordinary sugar) does not ferment. If boiled with acid it is *inverted,* as indicated by the following equation:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

when fermentation may take place.

the products, through the lime-water. This action should be allowed to continue for two days, then decant the liquid upon a filter. Set up a condenser and a distilling flask; place the filtrate together with several "boiling tubes" in the distilling flask; insert a thermometer in a hole in the cork with which the distilling flask is provided, so that the bulb just touches the surface of the contents of the flask; heat gently, and collect that portion of the distillate which passes over between 80° and 93° C.

(*b*) Notice the odor of the distillate (?). Place a few drops of it on a watch glass and ascertain whether it burns (?). Test its reaction with litmus paper (?).

(*c*) Repeat (*b*), using (*a*) ethyl alcohol, (*b*) methyl alcohol (?). What are your conclusions as to the nature of the distillate used in (*b*)? What is its empirical formula? Its rational formula?

(*d*) Try the solubility of iodine, camphor, rosin, shellac, etc., in separate portions of alcohol (?).

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2\overline{CO}_2.$$

Ethyl alcohol, C_2H_5OH, is the best-known member of the class of alcohols. When pure, it is a transparent, colorless, mobile and volatile liquid possessing a peculiar and agreeable odor. It has a sp. gr. of 0.797, boils at 78.3° C., solidifies at —130° C., is of a neutral reaction, and burns with a non-luminous flame. When mixed with water a contraction of volume occurs and heat is liberated. The attraction of alcohol and water for one another is so great, that strong alcohol abstracts it from tissues, membranes, and other similar substances immersed in it; to this property are due its coagulating action on albumin and its preservative action on animal substances. Pure alcohol taken internally acts poisonously; when taken in the dilute form it possesses intoxicating properties. It is affirmed by various authorities that "it lowers the temperature of the body from 0.5° to 2° C., although the sensation of warmth is experienced."

Alcohol which does not contain more than 1 per cent. of water is known as *pure* or *absolute* alcohol. Diluted alcohol, made by mixing equal volumes of water and alcohol, has a sp. gr. of 0.936 and is identical with the *proof-spirit* of the United States Custom-house and Internal Revenue service.

Alcohol is an excellent solvent for many organic and inorganic substances. These alcoholic solutions are given such names as *spirits*, *tinctures*, *fluid extracts*, etc. The terminology depends on various pharmaceutical relationships. "Spirits from the pharmaceutical point of view, are simply *alcoholic* solutions of *volatile* substances." "The active ingredient may be solid, liquid or gaseous." "Tinctures are alcoholic solutions of medicinal substances. They differ from spirits in being made from *non-volatile* bodies—the tincture of iodine being the one officinal exception to this rule." "Fluid-extracts are liquid alcoholic preparations of uniform and definite strength, made by percolating drugs with menstrua, and concentrating a portion of the percolate so that in each case a cubic centimeter represents the medicinal virtues of one gram of the drug; they are mostly concentrated tinctures."—"Practice of Pharmacy."—Remington.

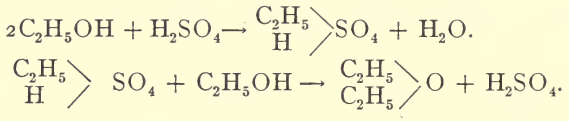
Experiment IV.—Tests for Ethyl Alcohol.

(*a*) Iodoform test. Dissolve a small flake or crystal of iodine in 2 or 3 cm.^{3} of alcohol; add a strong solution of crystallized sodium carbonate or potassium hydroxide until the brown color of the solution disappears; the yellow precipitate which forms is iodoform, CHI_3.

Note.—The student is reminded that other alcohols, acetone, aldehyde, etc., show the same reaction.

(*b*) Aldehyde test. Reducing action of alcohol. To 4 or 5 cm.^{3} of a potassium dichromate solution add 1 cm.^{3} of sulphuric acid and 2 cm.^{3} of alcohol; heat the solution gently and note the odor of the gaseous product, acetic aldehyde (C_2H_4O), which is a volatile liquid boiling at 20.8° C. The green color of the solution is due to the formation of chromium sulphate, $Cr_2(SO_4)_3$.

(*c*) Ether test. Add to 2 cm.^{3} of alcohol the same volume of strong sulphuric acid; heat to boiling and add a little more alcohol, drop by drop. The odor of ethyl ether, $(C_2H_5)_2O$, may be easily detected on further heating.



$$2C_2H_5OH + H_2SO_4 \rightarrow \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle SO_4 + H_2O.$$

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle SO_4 + C_2H_5OH \rightarrow \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O + H_2SO_4.$$

(*d*) Ester test. To 4 or 5 cm.^{3} of a strong solution of sodium acetate, $NaC_2H_3O_2$, add a few drops of concentrated sulphuric acid and 5 or 6 drops of ethyl alcohol, then warm the mixture gently. Notice the pleasant fruit-like odor of the ester, ethyl acetate, a volatile liquid which is formed under the above conditions. The foregoing is a test for either alcohol or acetic acid.

$$\underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\text{Acetic acid.}}{C_2H_3O_2H} \rightarrow \underset{\text{Ethyl acetate.}}{C_2H_5C_2H_3O_2} + H_2O$$

$$C_2H_5OH + NaC_2H_3O_2 + H_2SO_4 \rightarrow C_2H_5C_2H_3O_2 + NaHSO_4 + H_2O.$$

In many of their relations the alcohols are analogous to metallic hydroxides. For example, CH_3OH and C_2H_5OH are compounds analogous to NH_4OH, KOH, NaOH, etc. Both classes of compounds react with acids to form salts. Ethyl acetate, one of the products of the interaction of ethyl alcohol and acetic acid, is an organic salt analogous to ammonium or sodium acetate. These organic salts are often called *esters* or *ethereal salts*. The latter term is unfortunate as these salts do not ionize to any extent and possess practically none of the properties of ordinary salts.

Experiment V.—Properties of a Trihydric Alcohol (Glycerine or Glycerol).

Place a little glycerine in a test tube. Note its color and odor (?). Taste a drop of it (?). Rub a little of the glycerine between the fingers (?). Test it with litmus paper (?). Ascertain its solubility in (*a*) water, (*b*) alcohol, (*c*) ether and (*d*) chloroform (?).

Heat a little glycerine in a dry test tube and try to boil it. What evidence have you that it undergoes decomposition? Can glycerine be distilled by itself? How may it be distilled (volatilized)? Enumerate several of its uses. Write the rational formula for glycerine.

Glycerine (glycerol), $C_3H_5(OH)_3$, is an alcohol containing three hydroxyl groups. It is the trihydric or triatomic alcohol of the radical glycerl, C_3H_5, formed by the removal of three atoms of hydrogen from the saturated hydrocarbon, propane (C_3H_8), and combination of the radical with three hydroxyl groups. The common animal and vegetable fats and oils contain glycerine in combination with the *fatty* acids. These compounds form a class of *esters* known as *glycerides*, which when treated with alkalies undergo decomposition—the fatty acids combining with the metals of the alkali to form *soaps*, whilst glycerine is liberated.

Pure glycerine is a thick, colorless, odorless liquid, oily to the touch, hygroscopic, neutral in reaction and rather sweet. It is soluble in water and alcohol in all proportions, but insoluble in chloroform and ether. It has a sp. gr. of 1.225, and solidifies at low temperatures forming deliquescent crystals which melt at 17° C. When heated to the boiling-point, under ordinary atmospheric pressure, it undergoes decomposition; therefore, it cannot be distilled by itself. However, it can be distilled under diminished pressure and is volatilized in the presence of water or when hot steam is allowed to pass through it.

On account of its solvent properties glycerine is used extensively in the preparation of official solutions of various organic and inorganic substances. These solutions have been termed *glycerites*.

"*Nitro-glycerine*," $C_3H_5(NO_3)_3$ is prepared by treating glycerine with a mixture of concentrated sulphuric and nitric acids. The chemical action is indicated by the following equation:

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O — (— ?\ \text{cal.})$$

It is a pale-yellow oily liquid soluble in alcohol but insoluble in water; crystallizes at —20° C. in long needles and explodes very violently by concussion. It can be burned in an open dish, but if heated above 250° C. it explodes. One kilogram of nitro-glycerine yields after explosion about 725 liters of gas, measured at 0° C., and 760 mm. pressure. As the temperature of the gas is raised to about 7000° C. by heat liberated by the explosion, the volume is much larger than that suggested. The explosive power of nitro-glycerine is about thirteen times as great as that of gunpowder. Nitro-glycerine is the active constituent of a number of explosives. *Dynamite* is infusorial earth impregnated with nitro-glycerine. While it is not readily exploded by pressure or jar, it is by percussion.

Experiment VI.—Properties of Phenol (Carbolic Acid). Tests.

Caution.—Phenol is strongly poisonous,* and causes blisters if it comes in contact with the flesh.

(*a*) Ask the instructor to show you a specimen of solid phenol or a solution of it. Observe its empyreumatic and disagreeable odor. When diluted greatly, it possesses a sweetish and afterward a caustic taste. Test a dilute solution with litmus paper (?). Recall its solubility in water (See Exp. XI, "Solutions"). What peculiar property of solubility in water does it possess? Define "critical solution temperature." What is the melting point of phenol? Indicate by rational formula that phenol (phenyl hydrate) has the structure of an alcohol.

(*b*) To 2 cm.^{3} of phenol add small quantities of a solution of potassium hydroxide until the phenol is in solution. What are the products of the interaction? Now add an excess of hydrochlorid acid. Results? Equations?

(*c*) Tests.

1. Add a few drops of a neutral solution of ferric chloride to an aqueous solution of phenol. A beautiful blue color is imparted to the solution.

2. Bromine water added in excess gives a yellowish-white precipitate of tri-brom-phenol, $C_6H_2Br_3OH$, which has been used medicinally under the name of "bromol."

3. When phenol is heated with nitric acid it turns yellow owing, to the formation of *picric acid* (trinitro-phenol), $C_6H_2(NO_2)_3OH$.

Phenol (carbolic acid, phenyl hydrate, phenyl alcohol), C_6H_5OH, is prepared by the distillation of coal tar.† It is one of the chief constituents of the distillate obtained between 170°–190° C. When the distillate is chilled the *naphthalene* crystallizes out, leaving the phenol mixed with various neutral oils and impurities.

The remaining liquor is treated with an alkali which dissolves the phenol, forming a solution of "sodium carbolate" which separates by gravity from the undissolved neutral oils. From the solution it is precipitated by sulphuric acid, carbon dioxide or furnace gases—the crude carbolic acid separating as an oily liquid. It is purified by repeated distillations and crystallizations.

Pure carbolic acid is obtained in the form of colorless, interlacing, needle-shaped crystals which sometimes acquire a pinkish tint. The presence of water prevents it from solidifying. It melts at 43° C. and boils at 183° C. The sp.gr. is 1.065. It is very soluble in alcohol,

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* *Antidote.*—Castor oil, or olive oil, or a mixture of both, or a mixture of magnesia and oil, also sodium sulphate (Glauber's salt), internally and hypodermically are used as *antidotes.*

† Thorpe's Outlines of Industrial Chemistry.

ether and glycerine. At 17° C., it dissolves in 20 parts of water. It also dissolves a small amount of water; therefore if phenol is shaken with less than 20 parts of water at 17° C., the mixture will separate into an upper layer containing about five per cent. and a lower layer containing about seventy-five per cent. of phenol. At or above 68.9° C., the two are miscible in all proportions. (Recall Exp. XI, "Solutions.") It is very poisonous and a very powerful disinfectant or germicide.

Phenols are the hydroxyl derivatives of benzene, C_6H_6. Their constitution allies them with the alcohols, but they possess properties so different from those of the alcohols of the methane and ethylene series that they have been given the general but distinctive name by which they are now known. They differ from the common alcohols in not yielding aldehydes or acids by oxidation. Although phenol is generally called carbolic acid, it has a neutral or but faintly acid reaction. It combines with strong bases to form a class of salts known as the *carbolates* or *phenolates*.

$$\underset{\text{Phenol}}{C_6H_5OH} + NaOH \rightarrow \underset{\substack{\text{Sodium}\\\text{Carbolate}}}{C_6H_5ONa} + H_2O.$$

$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\substack{\text{Salicylic}\\\text{Acid}}}{HC_7H_5O_3} \rightarrow \underset{\text{Salol}}{C_6H_5 . C_7H_5O_3} + H_2O.$$

$$\underset{\text{Phenol}}{2C_6H_6O} + \underset{\substack{\text{Phthalic}\\\text{anhydride}}}{C_8H_4O_3} \rightarrow \underset{\substack{\text{Phenol-}\\\text{phthalein.}}}{C_{20}H_{14}O_4} + H_2O.$$

Experiment VII.—Preparation and Properties of Ether.

Caution.—In working with ether carefully avoid the neighborhood of free flames as its vapor is easily ignited.

(*a*) Preparation. Recall or repeat Exp. IV (*c*). Equation?

(*b*) Pour a few cm.^{3} of ether into a test tube. Observe its color, odor and volatility (?). Is it lighter or heavier than water? Taste a drop of it (?). Allow a few drops to fall upon the back of the hand (?). Pour a drop upon a watch glass. Does it evaporate more or less rapidly than alcohol? Predict its boiling-point relative to that of alcohol (?). Reasons for your answer? Test the ether with litmus paper (?). What can you say with reference to the mutual solubility of ether and water? (Recall Exp. X, "Solutions.")

To a small piece of resin or wax add several cm.^{3} of ether (?). The result is typical. What are your conclusions as to its solvent properties? Write the rational formula for ether (ethyl). To what class of inorganic compounds is it analogous?

Our ordinary *ether* (ethyl ether) is the representative of a very large class of organic compounds which are given the general name of *ethers*. These compounds are the oxides of the organic radicals and are analogous to the various metallic oxides. Many ethers are products of vegetable life, and have generally a characteristic and pleasant odor. Fruit essences consist mainly of *compound ethers* (esters). That which is known as the "bouquet" or "flavor" of wine and other alcoholic liquors is due chiefly to ethers or compound ethers, which are formed during the various stages of fermentation by the action of the acids present upon the alcohol or alcohols formed. The improvement which such alcoholic liquids undergo "by age" is caused by a continued chemical action between the substances named. Pure ethyl ether is a colorless, mobile liquid which has a sp.gr. of 0.718 at 156° C. It boils at 34.6°. On account of its volatility, ether should be kept in strong bottles tightly corked. It is easily combustible and burns with a luminous flame. Ether mixes with alcohol in all proportions. Official ether contains 96 per cent. of ethyl ether and 4 per cent. of alcohol. It is stated by Noyes (W. A.) that ether "dissolves in 11.1 volumes of water at 25° C., while it will in turn dissolve one-fiftieth of its volume of water." It is a good solvent for fats, alkaloids, resins and many other classes of organic compounds. It is used extensively as an anesthetic, causing intoxication and finally loss of consciousness and sensation when inhaled. It is neutral in reaction.

Experiment VIII.—Oxidation of an Alcohol to an Aldehyde.

(*a*) Acetic or ethyl aldehyde. Recall or repeat Exp. IV (*b*). Equation?

$$\begin{array}{lcl} C_2H_6O & -2H \rightarrow & C_2H_4O \\ \text{Ethyl} & & \text{Acetic} \\ \text{alcohol} & & \text{aldehyde.} \end{array}$$

(*b*) Formic aldehyde or formaldehyde. This substance is produced by passing a mixture of the vapor of methyl-alcohol and air over a heated copper spiral. The experiment may be performed as follows: Pour 5 cm.^{3} of methyl-alcohol into a test tube clamped in a vertical positon—then drop into the alcohol a spiral of copper wire which has been heated to redness in a flame. The colorless penetrating gas which is evolved is formaldehyde. What is the formula for formaldehyde?

$$CH_3OH + O \rightarrow H,CHO + H_2O.$$

Aldehydes are formed by the removal of hydrogen from alcohols. In fact, the name *aldehyde* is derived from *alcohol dehydrogenatum* which refers to its method of formation. The removal of hydrogen may be accomplished by various methods, as, for example, by the oxidation of alcohols, when one atom of oxygen combines with two atoms of hydrogen, forming water, while an aldehyde is formed simultaneously. The realtions in *composition* of the alcohols, aldehydes and acids are shown by the following formulæ:

Radicals	Hydrocarbons	Alcohols	Ethers	Aldehydes	Acids
CH_3	CH_4	CH_3OH	$(CH_3)_2O$	CH_2O	CH_2O_2
C_2H_5	C_2H_6	C_2H_5OH	$(C_2H_5)_2O$	C_2H_4O	$C_2H_4O_2$

Aldehydes, when further oxidized, are converted into acids. Many of the aldehydes in consequence of their tendency to unite with oxygen to form acids are strong reducing agents. Only a few of the aldehydes are of practical interest, as, for examples, formaldehyde (CH_2O or $H.COH$), acetaldehyde (C_2H_4O or $CH_3.COH$), the polymerized form of acetaldehyde, paraldehyde ($(C_2H_4O)_3$) and a few others.

Formaldehyde is a gas at ordinary temperatures but may be condensed to a liquid which boils at —21° C. It is readily soluble in water, and a 40 per cent solution has been placed on the market under the name of *formalin.* This same name is now given to solid paraformaldehyde, $(CH_2O)_3$, which is a polymerized form of formaldehyde. It is extensively used as an antiseptic. The paraformaldehyde (formalin) splits up into three molecules of formaldehyde, which, escaping as a gas, is used for disinfecting purposes. It does not act injuriously on the fabric or color of household goods, thus possessing an advantage over chlorine and sulphur dioxide.

Experiment IX.—Organic Acids. Acetic Acid.

(*a*) To a solution of sodium acetate, $NaC_2H_3O_2$, add a little dilute sulphuric acid. Observe the odor—it may be necessary to gently warm the mixture (?). Equation? Name two commercial processes by which acetic acid is manufactured.

(*b*) Test a solution of acetic acid with litmus paper (?). Pour a few drops of the solution upon a solution of sodium carbonate, Na_2CO_3. Results? Equation? What per cent. is ionized in a 1 N solution? In a .1 N solution? (See table). Would you infer that it is a "strong" or a "weak" acid? Test its relative electrical conductivity (?). What class of salts are formed by acetic acid?

(*c*) Compare the odor of dilute acetic acid with vinegar (?). Try the action of vinegar upon a solution of sodium carbonate (?). Equation? What are your conclusions as to the relation of acetic acid to vinegar?

(*d*) Tests for acetic acid.

1. Acetates heated with sulphuric acid evolve acetic acid which may be readily detected by its odor.

2. Acetates or acetic acid heated with sulphuric acid and alcohol yield the characteristic odor of ethyl acetate. (See Exp. IV. (*d*)).

3. Ferric chloride, when added to a solution containing acetic acid or an acetate carefully neutralized, gives ferric acetate, which is a soluble salt and imparts a dark red color to the solution. When this solution is boiled, a brownish precipitate of basic ferric acetate separates out.

As suggested previously, many organic acids are produced by the oxidation of alcohols. They show the characteristics mentioned of inorganic acids, viz., when soluble, have an acid or sour taste, redden litmus, contain hydrogen which is replacable by metals with the formation of salts, and yield hydrogen ions. The greater number of these organic acids possess these acid properties in a much less marked degree; in fact, they are so weak that the acid properties can often be scarcely detected. Most organic acids are colorless, odorless solids; a few are liquids and scarcely any are gaseous at the ordinary temperature.

Pure *acetic acid*, or *glacial acetic acid*, melts at 16.7° C. and boils at 120° C. It has a sp. gr. of 1.055. It causes blisters on the skin and is miscible in water, alcohol and ether. It forms salts known as acetates, all of which are soluble in water. (See Thorpe's "Outlines of Industrial Chemistry" and Sadtler's "Industrial Organic Chemistry" for the manufacture of acetic acid.)

Experiment X.—Tartaric Acid. Tests.

(*a*) Examine some crystals of tartaric acid. Is it soluble in water? What is the effect of the solution on blue litmus paper? Try the effect of an aqueous solution of tartaric acid upon a solution sodium bicarbonate (?). Equation?

(*b*) Give the formula and state one well-defined use of each of the following: cream of tartar, Rochelle salt, tartar emetic.

(*c*) Tests.

1. Tartrates are readily charred by heating them with strong sulphuric acid.

2. Tartrates are decomposed (char), and evolve an odor resembling that of burnt sugar when heated.

3. Silver nitrate gives with a neutral solution of a tartrate a white precipitate of silver tartrate which *blackens* on boiling in consequence of the decomposition of the salt, with separation of silver. If ammonium hydroxide is added before boiling, *a mirror of metallic silver* will form upon the glass.

Tartaric acid, $H_2C_4H_4O_6$, is frequently found in vegetables and fruits, and especially in grapes. With the exception of the tartrates of the alkalies, all normal tartrates are either insoluble or difficultly soluble. Most of the insoluble tartrates dissolve in tartaric acid forming "acid" salts.

Experiment XI.—Oxalic Acid. Tests.

Caution.—Oxalic acid is a poison.

(*a*) Repeat Exp. X (*a*), substituting oxalic acid for tartaric acid.

(*b*) Place 5 grm. of sugar in 150 cm.^{3} flask; add 50 cm.^{3} of nitric acid (1 – 1); heat gently in the hood until brown fumes are given off, then remove the flame. When the brown fumes cease to escape, boil the liquid down rapidly to about 10 or 15 cm.^{3}; pour the solution into a crystallizing dish. Crystals of oxalic acid separate on cooling. Remove the crystals and dissolve them in warm water and recrystallize them. Dissolve some of these crystals in water, and add this solution to a few cm.^{3} of a dilute solution of potassium permanganate which has been acidulated with a few drops of sulphuric acid. Is the permanganate decolorized? Equation?

(*c*) Tests.

1. When strong sulphuric acid is heated with oxalic acid or oxalates carbon monoxide and carbon dioxide are evolved.

2. Calcium chloride gives with neutral solutions of oxalic acid a white precipitate of calcium oxalate, CaC_2O_4, which is soluble in hydrochloric, but insoluble in acetic acid.

Oxalic acid, $H_2C_2O_4$, is a white solid, soluble in water, crystallizing from the solution with two molecules of water of crystallization, $H_2C_2O_4$, $2H_2O$. It occurs very widely distributed in the vegetable kingdom, as in certain plants of the *oxalis* varieties, in the form of the acid potassium salt. It may be obtained by the oxidation of many organic substances, chiefly sugars, starches, etc., by nitric acid or other strong oxidizers. It is prepared technically by heating sawdust or wood-shavings with a mixture of caustic soda and caustic potash to about 250° C., when the oxalate of these metals are formed. The mass is extracted with water, and the solution evaporated to crystallization, when sodium oxalate is deposited or the dissolved alkali oxalate is treated with calcium hydroxide, insoluble calcium oxalate forming. The calcium oxalate is decomposed by sulphuric acid.

Oxalic acid is probably the strongest organic acid. It is dibasic and acts as a reducing agent, decolorizing solutions of the permanganates. It possesses poisonous properties.*

Oxalic acid is largely used in dyeing, calico-printing and bleaching, in cleaning brass and in removing iron-mould from linen.

The oxalates of the alkalies are soluble in water. All other oxalates are insoluble or only sparingly soluble.

Experiment XII.—Halogen Derivatives. Iodoform. Chloroform.

(*a*) Iodoform. Recall or repeat Exp. IV (*a*). Equation?

(*b*) Chloroform. The following method for its preparation is suggested by Remsen: Mix 550 grams of bleaching powder and 1.25 liters water in a 3-liter flask. Add 33 grams alcohol of sp. gr. 0.834. Heat gently on a water bath until action begins. A mixture of alcohol, water and chloroform will distill over. Add water and remove the chloroform by means of a pipette. Add calcium chloride to the chloroform and, after standing, distill on a water bath.

$$4C_2H_6O + 8\,Ca(ClO)_2 \rightarrow 2CHCl_3 + 3(Ca(CHO_2)_2) + 5CaCl_2 + 8\,H_2O.$$

(*c*) Note the odor of pure chloroform. Taste a drop of it (?). Test its reaction with litmus paper (?). Shake a little chloroform with a few $cm.^3$ of a solution of silver nitrate (?). Name one of the principal uses of chloroform.

(*d*) Tests for chloroform.

1. Add a few drops of chloroform to 5 $cm.^3$ of Fehling's solution and heat; red cuprous oxide is thrown down.

2. A strip of filter paper saturated with chloroform burns with a green-mantled flame which emits vapors of hydrochloric acid. The

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* *Antidote.*—"Lime-water or calcium carbonate should be administered, but no alkalies as in cases of poisoning by mineral acids, because alkali oxalates are soluble."—Simon's Manual of Chemistry.

acid vapors may be rendered more visible by approaching the flame with a glass rod moistened with ammonium hydroxide.

Chloroform is a heavy, colorless liquid, possessing a sp. gr. of 1.526 at 0° C.; it has a burning sweet taste; a neutral reaction, a boiling-point of 61.2° C., and a melting-point of —70° C. It is very slightly soluble in water, but miscible with alcohol and ether in all proportions. Pure chloroform is not very stable. It undergoes decomposition slowly when exposed to light and air, yielding hydrochloric acid, free chlorine, phosgene ($COCl_2$) and other products. Some of the decomposition products are more poisonous than chloroform, therefore when the latter is used as an *anesthetic* it is essential that the chloroform should be *pure*. It has been found that the presence of a small amount (.5 to 1%) of alcohol renders the chloroform more stable. Commercial chloroform usually contains a small quantity (the U. S. P. allows one-half to one per cent.) of alcohol for this purpose; thereby changing the sp. gr. to about 1.488. Pure chloroform should not give more than a faint opalescence when shaken with a silver nitrate solution.

Experiment XIII.—Esters. Ethyl Acetate.

Recall or repeat Exp. IV (*d*). Equation?

Recall the note following Exp. IV. The *esters* are analogous to inorganic salts in structure, and it is frequently convenient to refer to them as "organic salts," but their resemblance to said salts ceases, however, with structure. The esters react very slowly. Originally, the esters were called "compound ethers"; for example, ethyl acetate was called "acetic ether." The terms are still occasionally employed.

All true *fats* are esters of the triatomic alcohol, glycerine, and the higher members of the fatty acids. They are frequently termed *glycerides;* stearin, for example, being the glyceride of stearic acid. Fats are widely distributed in the animal and vegetable kingdoms. They are found in animals generally under the skin, around the intestines and on the muscles, while in plants they exist chiefly in the seeds.

Human fat, *lard*, *mutton fat* and *beef tallow* are mixtures of *palmitin*, $C_3H_5(C_{16}H_{31}O_2)_3$, *stearin*, $C_3H_5(C_{18}H_{35}O_2)_3$, and *olein*, $C_3H_5(C_{18}H_{33}O_2)_3$.

Butter consists essentially of the glycerides of butyric acid, caprylic acid, caproic acid and capric acid which are volatile with steam, and of palmitic and stearic acids, which are not volatile. Palmitin and stearin are solids, but olein is a liquid at ordinary temperatures. The relative amount of these three fats determines its solid or liquid condition. The chief constituent of liquid fats is generally olein. The liquid fats have been given the name *fatty oils* or *fixed* oils in contradistinction to the *essential* or *volatile oils* which give the peculiar odors to plants. Among the more familiar essential oils are *spirits of turpentine*, *camphor*, *menthol*, *cedar oil*, *oils of cloves*, *lemon*, *mustard*, *peppermint*, *and wintergreen*, *attar of roses*, etc.

The taste and color of fats are due to foreign substances which are often produced by slight decomposition. Pure fats are odorless, colorless and tasteless substances which stain paper permanently. They are lighter than water and insoluble in it, sparingly soluble in alcohol, easily soluble in ether, carbon disulphide, benzene, etc. Fats heated above 300° C. decompose with the formation of various products, some of which possess a very disagreeable odor. Among the products is the aldehyde, *acrolein*, C_3H_4O.

Many of the pure fats keep without change, but since the greater number contain impurities, such as albuminous matter, etc., they suffer decomposition,* which results in a liberation of the fatty acids. The latter impart their odor and taste to the fats, causing them to become what is generally termed *rancid*.

Drying oils are a class of fats containing *unsaturated* acids which undergoing oxidation, render them hard. The principal vegetable drying oils are *linseed oil*, *hemp oil*, *poppy oil* and *sunflower oil*.

Among the vegetable *semi-drying oils* are *corn* or *maize oil*, *cotton-seed oil* and *castor oil*.

The vegetable *non-drying oils* of importance are *olive oil*, *peanut oil*, *palm oil*, *cocoanut oil* and *almond oil*.

Butterine and *oleomargarine* are perfect substitutes for common butter when the essential attributes are considered. They are made from mixtures of animal and vegetable oils flavored with a relatively small quantity of butter and colored to imitate it. Oleo oil from tallow and lard are largely used. These are frequently mixed with cotton-seed oil in cold weather to increase the percentage of olein.

Experiment XIV.—Preparation of Soaps. Glycerine.

(*a*) Preparation of soda soap. Put about 10 grams of lard or tallow in a 300 cm.^{3} Erlenmeyer flask; dissolve 4 grams of NaOH in 100 cm.^{3} of water, pour this solution into the flask; heat the mixture over a wire gauze until it ceases to foam, then add an equal volume of a saturated solution of sodium chloride. Stir constantly during the addition of the salt solution. Boil for a few minutes. Allow the mixture to stand until it separates into an upper solid zone or crust and a lower liquid zone which may be more or less colored. The solid layer is a mixture of *soda-soap* and unsaponified fat; the liquid contains *glycerine*, salt and various impurities. Drain off this liquid and add 3 grams of NaOH dissolved in 75 cm.^{3} of water; heat as previously directed until the mixture becomes adhesive. Pour the mixture into an open dish. The solid product should show the essential properties of *hard soap*. Equations? Explain the precipitation ("salting out") of the soap by means of sodium chloride.

(*b*) Preparation of potassium soap. Dissolve 5 grams of KOH in 100 cm.^{3} of alcohol; add 7 grams of lard; heat the mixture on a water bath until it has the consistency of syrup and the odor of alcohol is no longer perceptible. The mixture should be stirred constantly while it is being

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* A kind of fermentation which is aided by oxidation.

heated. Pour the mixture into an open dish and allow it to cool. The jelly-like product is *soft soap*. The alcohol is used as a common solvent for the fat and alkali.

$C_3H_5(C_{16}H_{31}O_2)_3$ Palmitin (Fat)	$+ 3NaOH \rightarrow$	$3NaC_{16}H_{31}O_2$ Sodium palmitate (Hard soap)	$+ C_3H_5(OH)_3$ Glycerin
$C_3H_5(C_{18}H_{35}O_2)_3$ Stearin (Fat)	$+ 3NaOH \rightarrow$	$3NaC_{18}H_{35}O_2$ Sodium stearate (Hard soap)	$+ C_3H_5(OH)_3$ Glycerin
$C_3H_5(C_{18}H_{33}O_2)_3$ Olein	$+ 3NaOH \rightarrow$	$3NaC_{18}H_{33}O_2$ Sodium oleate	$+ C_3H_5(OH)_3$ Glycerin
$C_3H_5(C_{16}H_{31}O_2)_3$ Palmitin	$+ 3KOH \rightarrow$	$3KC_{16}H_{31}O_2$ Potassium palmitate (Soft soap)	$+ C_3H_5(OH)_3$ Glycerin

Experiment XV.—Properties of Soaps.

(*a*) Dissolve a little of the soap prepared in Exp. XIV (*a*) in warm water; filter. To one-half of the filtrate add hydrochloric acid and shake vigorously. Observe that the fatty acids separate as solids and rise to the top. Remove this floating coagulum and test its solubility in alkali (?). Equations?

(*b*) To the other half of the soap solution add a calcium sulphate or magnesium sulphate solution. Note the formation of the corresponding insoluble calcium or magnesium salt of the fatty acid. Equations? Explain how the efficiency of soap is diminished by using it with *hard water*. What information do we convey by the expression *soft water*?

(*c*) Test yellow soaps, toilet soaps, etc., for free alkali. Tabulate your results giving the name of the soap used.

As previously explained, the common fats, glycerides or esters undergo decompostion when boiled with water, acids or alkalies with the formation of the free acid or a salt of the acid, and the alcohol (glycerin). This process of decomposing an ester is called *saponification*. The metallic salts which are formed when the saponification is effected by means of an alkali are called *soaps*. They are defined as *metallic salts of certain non-volatile fatty acids*. Soaps intended for washing purposes should contain only *soluble salts* of the acids; i.e., those of sodium or potassium; the magnesium, calcium, lead and other heavy metal salts are insoluble in water. The alkalies which are most frequently used in the manufacture of soaps are sodium and potassium hydroxides. The former yields a "hard soap"; the latter, a "soft soap" which is liquid under ordinary conditions because of a greater solubility and a lower melting-point. It is also probable that the greater deliquescence of the potassium soaps contributes to their "softness."

Experiment XVI.—Carbohydrates. Grape Sugar (Glucose).

(*a*) Examine some glucose (grape sugar) and tabulate its properties. What is its formula?

(*b*) Glucose ferments. Recall or repeat Exp. III (*a*). Equation?

(*c*) "Fehling's Test" for glucose. Place about 10 cm.^{3} of Fehling's solution in a test tube; add a few drops of a solution of glucose; boil hard for several minutes, then add a little more of the glucose solution. Continue to boil until on removing the tube from the flame, a dark-red precipitate settles to the bottom, leaving a clear colorless liquid. The red precipitate is cuprous oxide. This reaction can be used both for detection and quantitative determination, if other reducing substances are absent.

Experiment XVII.—Carbohydrates. Cane sugar (Saccharose). Inversion of Cane Sugar.

(*a*) Repeat Exp. XVI (*a*), substituting cane sugar or beet sugar for glucose.

(*b*) Cane sugar does not ferment. Repeat Exp. XVI (*b*) substituting cane sugar or beet sugar for glucose. Results?

(*c*) Inversion of cane sugar. Prepare a dilute solution of pure cane-sugar (rock-candy). Divide it into two parts. Test one portion with Fehling's solution as in Exp. XVI. Result? Now add a few drops of concentrated hydrochloric acid to the other portion of the sugar solution; heat for thirty minutes or longer, on a water bath at 100° C.; make the solution exactly neutral with a solution of sodium carbonate and test with Fehling's solution. Results? Conclusion relative to the presence of glucose? Equation? What is the function of the hydrochloric acid?

Experiment XVIII.—Carbohydrates. Preparation and Properties of Cellulose. Parchment Paper.

(*a*) Treat a small quantity of cotton-wool or Swedish filter paper successively with ether, alcohol, water, a caustic alkali, and finally, a dilute acid. Wash with water (?). Enumerate some of the properties and uses of cellulose. What is its formula?

(*b*) Parchment paper. Immerse a strip of filter paper in a solution prepared by adding 3 cm.^{3} of concentrated sulphuric acid to 15 cm.^{3} of water. Allow the paper to remain in the solution for about fifteen seconds, then remove it to a large vessel of pure water and wash it thoroughly. Rinse it in a very dilute solution of ammonia and dry it in the air. Result?

Experiment XIX.—Conversion of Cellulose into Glucose.

Cut a filter paper into small pieces and dissolve it in the least volume of concentrated sulphuric acid; add 500 cm.^{3} of water and boil for about an hour. Add pulverized chalk (calcium carbonate) to remove the sulphuric acid; filter, and evaporate the filtrate to small bulk. Test for glucose with Fehling's solution. Result? The chemical reaction may be indicated by the following equation:

$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \rightarrow \underset{\text{Glucose}}{n(C_6H_{12}O_6)}$$

Experiment XX.—L. T. Cellulose Nitrate (Gun-cotton or Smokeless Powder).

(*a*) Mix 1 volume of nitric acid which has a sp. gr. of 1.4 with three volumes of concentrated sulphuric acid; cool the mixture to about 12° C.; add as much pure cotton, small quantities at a time, as can be submerged in the acid mixture. Let the cotton remain in the mixture for twenty-four hours, then remove it and wash it several times in large volumes of water. Let it dry in the air. The white, friable mass which is very unstable is gun-cotton. To a small quantity of the prepared explosive touch a lighted match (?).

$$2(C_6H_{10}O_5) + 6HNO_3 \rightarrow C_{12}H_{14}O_4(NO_3)_6 + 6H_2O^*$$

Decomposition on explosion:

$$C_{12}H_{14}O_4(NO_3)_6 \rightarrow 7\overline{CO}_2 + 6\overline{CO} + 5\overline{N} + 8\overline{H} + 3H_2O + 1074\ \text{cal.}^\dagger$$

(*b*) State briefly the composition, preparation and uses of each of the following: cordite, celluloid and collodion.

Experiment XXI.—Carbohydrates. Properties of Starch.

(*a*) Dust a glass slide with starch, then examine the starch through a microscope. Make a diagram of the "field of vision."

(*b*) Ascertain if starch is appreciably soluble in cold water or alcohol (?). In hot water (?).

(*c*) Test for starch. Recall test for iodine (?).

(*d*) Cut a very thin section from a piece of potato by use of a microtome or a razor; float the section in a small dish of water to which has been added a few drops of an iodine solution. Remove the section from the water and spread it upon a glass plate, then cover it with a "cover glass." Examine the section through a microscope. Draw a diagram of what you see.

Experiment XXII.—Conversion of Starch into Glucose.

(*a*) Test a little starch paste with Fehling's solution (?).

(*b*) To 100 cm.^{3} of starch paste add 5 cm.^{3} of concentrated sulphuric acid; heat the mixture on a steam bath for two hours or until iodine no longer causes a blue color (which shows complete conversion of starch into either dextrin or glucose), and until 1 cm.^{3} of the solution yields no precipitate when 5 cm.^{3} of alcohol are added to it, dextrin being precipitated by alcohol. The dextrin should be converted into glucose.

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* Guttmann, Industrie der Explosivstoffe.

† Berthelot.

If the flask containing the mixture is connected with an inverted condenser, it will avoid the necessity of replacing the water which would otherwise escape. Proceed from this point as in Exp. XIX. Results?

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \rightarrow \underset{\text{Glucose.}}{n(C_6H_{12}O_6)}.$$

Carbohydrates.—These compounds are found widely disseminated in the vegetable kingdom; in fact, no other organic substances are found in such abundance. They are also found as products of animal life, as, for example, the sugar in milk.

Most carbohydrates are white, solid substances, generally soluble in water. Those belonging to the sugars have a more or less sweet taste. They are of neutral reaction, and are either fermentable or can, in most cases, be converted into substances capable of fermentation. Many of the carbohydrates, especially glucose, are easily oxidized; i.e., they are good reducing agents, as is shown in the foregoing experiments by the reduction in alkaline solution of the salts of copper (Fehling's solution).

The carbohydrates are now conveniently arranged under three heads. They are:

1. *Monosaccharides* or *simple sugars.*

This group contains those sugars which cannot be broken down into two or more sugars. Examples of these are glucose and fructose.

2. *Polysaccharides* or *complex sugars.*

Examples are cane sugar, sugar of milk and maltose.

3. *Polysaccharides, not resembling sugars.*

Examples are cellulose and starch.

Glucose.—$C_6H_{12}O_6$ (grape sugar, dextrose).—This substance is widely distributed throughout the vegetable kingdom, and is generally accompanied by fructose or fruit sugar. It is found in relatively large quantities in the juices of many fruits, such as the grape, fig, strawberry, cherry, mulberry, etc., and in honey. Traces (0.1 per cent. or less) of grape sugar occur in the liver, in the normal blood and in the urine. In the disease *diabetes mellitus*, the quantity secreted in the urine is greatly increased, frequently rising as high as 5 to 10 per cent. Glucose is easily prepared from pure cane sugar, which is easily hydrolyzed by the action of dilute acids, yielding glucose and fructose as indicated by following equation:

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Commercially, it is manufactured in large quantities by heating starch with dilute sulphuric acid, which converts the starch first into dextrin and maltose, and then into glucose. The solution obtained by this process is treated with chalk to remove the excess of acid, and filtered. The filtered solution is either evaporated to a syrupy consistency and sold as "glucose," or to dryness, the solid product obtained being known as commercial "grape sugar."

Glucose is soluble in water and alcohol. Its sweetness, compared with that of cane sugar, is as 3 to 5. It is fermentable and reduces Fehling's solution. It is optically active, turning the plane of polarization to the right. $(a)_D = +52.7°$ for a 10 per cent. aqueous solution which has been prepared for some time. Cold, freshly prepared solutions give a much larger rotation.

Saccharose, $C_{12}H_{22}O_{11}$ (cane-sugar, beet-sugar).—Sucrose (saccharose) is formed in the juices of many plants, but it is usually associated with substances which render its extraction exceedingly difficult and unprofitable. The sugar-cane, sugar-beet, sugar-maple and the date-palm are the commercially important sources of sugar, the first two supplying nearly all the sucrose of commerce.

Sucrose forms white, hard, crystalline granules, but may be obtained by crystallization from water in large monoclinic prisms (*rock-candy*). It is sparingly soluble in alcohol, but dissolves in 0.5 its own weight of water at temperatures below 20° C., and in 0.2 parts at 100° C.; it melts at 160–161°; and on cooling it solidifies to a pale-yellow, amorphous, glassy mass known as *barley sugar*, which after a long time becomes opaque and crystalline; when heated to 200–210° C., it loses water and is gradually converted into a brown, almost tasteless substance called *caramel*, which is used largely for coloring liquors, soups, etc. Oxidizing agents act energetically upon cane sugar, converting it into oxalic acid and saccharic acid; a mixture of cane sugar and potassium chlorate will deflagrate with explosive violence when moistened with a drop of sulphuric acid; an acid solution of potassium permanganate is decolorized (reduced) by sugar. Although sucrose is a strong reducing agent, it does not reduce Fehling's solution.

Pure sucrose does not ferment, but if a trace of a mineral acid is added to an aqueous solution and the liquid warmed or allowed to stand, the sucrose is hydrolyzed with the formation of equal quantities of the fermentable substances, glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6}.$$

Sucrose is optically active, $(a)_D = +66.51°$ at 20° C. for a solution containing 26.004 grams of sugar in a volume of 100 cm.³ Therefore, sucrose is *dextrorotatory*, i.e., rotates the plane of polarized light to the right, but when it has been hydrolyzed with acids as indicated by foregoing equation, the resulting solution of glucose and fructose is *levorotatory*, i.e., the plane of polarization has been reversed or "inverted." This is due to the fact that fructose* causes a greater rotation to the left than glucose does to the right. The mixture of glucose and fructose is called *invert sugar*, and the process of converting sucrose into these two forms is called *inversion*. An instrument known as the *saccharimeter* is used to determine the rotatory power of a known solution before and

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* $(a)_D = -93°$ in 10 per cent. aqueous solution.

after inversion, and from this data the percentages of cane sugar and invert sugar present in the sample can be calculated.

The ease with which sucrose is inverted indicates that the radicals of glucose and fructose, which it evidently contains, are united by oxygen. (See probable formula of sucrose, page 251.)

Cellulose $(C_6H_{10}O_5)_n$.—Cellulose is the principal constituent of cell membranes and of the woody fiber of plants, and constitutes, in fact, the framework of all vegetable tissues. Some parts of vegetables, such as cotton, flax and hemp, consist almost wholly of cellulose.

Pure cellulose is a white, transparent mass, insoluble in all the common solvents; it dissolves slowly in concentrated sulphuric acid, and if the solution be diluted with water and boiled, dextrine and finally glucose are produced. Hence, it is possible to convert wood into sugar.

Cellulose is used extensively in the manufacture of fabrics, paper and explosives.

Paper consists essentially of *cellulose fibers matted or felted into a coherent layer or sheet.* Usually it is "loaded" with mineral matter to give it weight and render it smooth and less porous.

Starch $(C_6H_{10}O_5)_n$.—Starch is found in abundance in the vegetable kingdom, occurring in nearly all plants in a greater or lesser quantity. It is found chiefly in the seeds, particularly of the cereals and the *leguminosæ*, but also in the roots and stems of many plants. It is formed in the leaves and green parts and then transported in soluble form to other parts of the plant where it is used to build up the tissues, or is deposited as reserve material. The details of the formation of starch are not fully understood, but it appears that chlorophyl acts like a "contact" substance or a "catalyser" in the reaction by which starch is formed in the plant. The carbon dioxide of the air is reduced by the joint action of sunlight (energy), and protoplasm and the chlorophyl, the carbon being assimilated, while a portion of the oxygen is set free. If the various stages in which the reaction takes place are disregarded, the ultimate chemical change may be represented by the following thermo-chemical equation:

$$6CO_2 + 5H_2O \rightarrow C_6H_{10}O_5 + 6O_2 - 671{,}000 \text{ cal.}$$

or

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2.$$

That substances of such a high molecular weight as starch or glucose should be formed directly, as indicated by above equations, is regarded by chemists as highly improbable. Baeyer* holds that formaldehyde, CH_2O, is the first reduction product of carbon dioxide in plants, and that glucose from which starch may be derived is formed by a polymerization process:

$$6CO_2 + 6H_2O \rightarrow 6CH_2O + 6O_2$$
$$6CH_2O \rightarrow C_6H_{12}O_6$$
$$C_6H_{12}O_6 \rightarrow C_6H_{10}O_5 + H_2O.$$

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* Berichte der deutchen chemischen Gesellschaft, 3, 67.

Starch as found in its natural condition possesses a granular structure, the granules differing from each other so markedly that the source from which they are derived can usually be determined by a microscopic examination. Each starch granule is made up of different layers, arranged abound a nucleus which is generally at one side of the granule. The interior substance of the granule consists of "granulose," while the transparent, inert and insoluble covering resembles cellulose* in structure.

Ordinary starch is a white, amorphous, tasteless substance, insoluble in water and alcohol, but if heated with water the granules swell and rupture the cell walls, when the "granulose" combines with water to form a jelly-like paste. If this paste is boiled with an excess of water it forms a partial solution or an emulsion, which passes readily through a filter paper. This solution yields a characteristic blue color with iodine, hence the use of the latter as an "indicator" in many analytical operations. Starch is *levorotatory* and is converted into dextrin or British gum by heating it in the dry condition to about 200° C. When boiled with dilute acids, starch is converted successively into dextrin, maltose and glucose. A process which is of the utmost importance in the manufacture of alcohol and spiritous liquors is the decomposition of starch at about 65° C. by the ferment *diastase* into dextrin and maltose:

$$3C_6H_{10}O_5 + H_2O \rightarrow C_6H_{10}O_5 + C_{12}H_{22}O_{11}.$$

Starch is an important article of food, especially when associated with albuminous substances, as in ordinary flour.

In the United States starch is manufactured principally from maize and wheat; in Europe, mainly from potatoes, but also from maize, wheat and rice.

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* "Recent investigations tend to prove that "starch cellulose" is not present as such in the granule, but is formed from starch substance by the action of acids or fermentation."—Thorpe.

CHAPTER XXII.

ALUMINUM FAMILY.

Boron, B, 11.0
(Aluminum, Al, 27.1)
(Earth metals,)

On inspecting the periodic table it will be seen that the fourth column contains the elements, **boron, aluminum** and a number of rare "earth metals." The two which are of particular interest to us in this work and are of the most importance are boron and aluminum. The relations of these two are very similar to those existing between carbon and silicon. While boron is usually classed with carbon and silicon on account of its close resemblance to these elements, the connection between boron and aluminum is plainly revealed in the similarity of their physical and chemical properties. Boron possessing the lower atomic weight, the metallic character is reduced or does not appear. It is a pronounced non-metal, and its oxide and hydroxide are almost exclusively acidic. Its properties approximate those of the metalloids. For this reason it is customary to treat boron with them, as suggested above.

Aluminum is really a perfect metal, and with its oxide and hydroxide the basic properties predominate. Although the hydroxide is capable of forming metallic salts with strong bases (alkalies) of the type of sodium aluminate Na_3AlO_3, yet owing to the higher atomic weight of aluminum the basic character exceeds the acidic. All the members of the aluminum family are trivalent.

Boron will be treated at this time while aluminum will be taken up in connection with the metals.

BORON, B.

At. Wt. 11.0 Sp. gr. 2.5–2.63.

As may be inferred from that which has preceded, **boron** occupies a rather isolated position among the metalloids, and may best be regarded as a transition element between this class and the metals. Although it seems expedient to classify boron with carbon and silicon, the elements which it resembles, especially in the free state, the student is reminded that the group of elements most nearly related to it must be sought for among the "earth metals."

The element boron has never been found in nature in the free state. It occurs most abundantly in combination as boric acid and as metallic borates, among which are *tincal* or crude borax, $Na_2B_4O_7$, *boracite* (magnesium salt) and *colemanite* or *borate spar*, $Ca_2B_6O_{11}$.

Boron is an infusible solid substance capable of existing in both the *amorphous* and *crystalline* forms. The former is a greenish-black powder which may be prepared by heating the oxide of boron, B_2O_3, with magnesium or sodium in a covered crucible. The fused mass is then boiled with hydrochloric acid. The boron is separated by filtration. Crystalline boron is obtained by the fusion of aluminum with boron trioxide. On account of its hardness, it is called "adamantine boron." When prepared by the above process, it is not quite pure. It contains a small quantity of aluminum which is probably isomorphous in this form with boron. The crystals are transparent, and in their luster and hardness they resemble the diamond. The amorphous variety is probably unstable with respect to the crystalline. The former has a sp. gr. of 2.5; the latter, 2.63.

Boron forms an unstable hydride (probably B_3H_3) which resembles stibine in its readiness to undergo decomposition. However, the two most important compounds of boron are boron trioxide and boric acid. Although the acid, H_3BO_3, is known in the free state, the salts of the acid are not known with any dergee of certainty. The salts are formed from the so-called "condensed" acids, which are intermediate products formed by the dehydration of orthoboric acid. This acid looses water when heated and passes into the anhydride, B_2O_3, which melts forming a glass-like mass. This fused substance is capable of dissolving the oxides of various metals, many of which impart characteristic colors to the "borax bead." These phenomena serve for the detection of such metals in analysis. The readily fusible alkali salts of boric acid are frequently employed for this purpose, and for cleaning surfaces to be soldered.

Boric acid is a very weak acid, the salts of which readily undergo hydrolysis when dissolved in water. An aqueous solution of the acid conducts electricity but slightly better than pure water.

Alcohol and boric acid interact forming the corresponding *ester* which is very volatile. If the alcohol is set on fire the ester imparts a green color to the flame. This reaction is frequently used for the detection of boric acid.

Boric acid (boracic acid) is used widely as an antiseptic and a as preservative.

Experiment I.—Preparation and Properties of Boron.

Preparation and properties similar to silicon. Repeat Exp. I, "Silicon," substituting boron for silicon, and boric oxide for sand or quartz. What is the valency of boron?

Experiment II.—Hydrolysis of Borates. Boric Acid. Dehydration of Boric Acid. Borax.

(*a*) Dissolve a little powdered borax (sodium tetraborate, $Na_2B_4O_7$)

in distilled water. Test the solution with neutral litmus paper. Result? Explain. Equation?

(*b*) Dissolve 20 grams of borax in 100 cm.^{3} of hot water. Add concentrated hydrochloric acid until the solution is strongly acid, then set it aside to cool. Results? Equation?

Filter and wash out the mother-liquor from the crystals with a little cold water. Dry some of the boric acid crystals by pressing them between filter paper. Test the solubility of the crystals in cold water (?). In alcohol (?). In hot water (?). Test this latter solution with litmus paper (?). Determine its electrical conductivity relative to water. What is its degree of ionization? (See tables.) What are your conclusions as to the nature of boric acid, H_3BO_3? Write the structural formula for H_3BO_3.

(*c*) Place about a gram of H_3BO_3 in a small porcelain crucible; heat gently at first, then strongly. Results? Equations indicating various stages in the dehydration?

(*d*) Dissolve 5 grams of H_3BO_3 and 6 grams of Na_2CO_3 in 15 cm.^{3} of hot water (?). Set the solution aside and allow it to evaporate slowly? Result? Equation? Enumerate some of the uses of borax. Its formula?

Experiment III.—Preparation and Use of Borax Beads. Solubility of Metallic Oxides in the Bead.

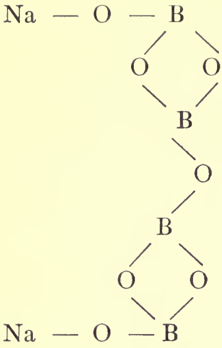
(*a*) Make a small closed loop on the end of a platinum test wire which has been previously sealed into a piece of glass tubing; heat the wire in the flame of a Bunsen burner and dip it into powdered borax; heat it in the flame until the white puffy mass shrinks to a small glass-like bead which should be transparent. If the bead is too small to fill the loop, add more borax and heat again. The bead may be removed by dipping it, while hot, into cold water; the sudden cooling shatters it.

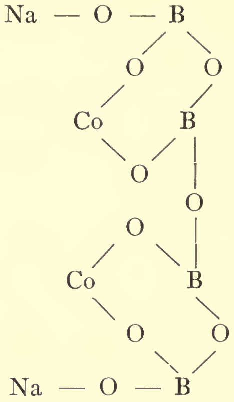
$$Na_2B_4O_7 \longrightarrow 2NaBO_2, B_2O_3.$$

(*b*) Moisten a "borax bead" with a cobalt chloride or nitrate solution. Heat the bead in the oxidizing flame. Notice the color of the bead when hot, also when it is cold (?). The color is usually detected by looking at the bead against a white object in a strong light. Is the color of the bead altered by heating it in the reducing flame?

(*c*) Repeat (*b*), substituting a copper sulphate solution for the cobalt solution. Tabulate results. Salts of the following may also be used: nickel, iron, manganese and chromium.

The following formulæ probably represent respectively the structures of borax, and the compound which is formed by the *union* of the metallic oxide and the fused borax.





COLORS OF BORAX BEADS.

Metal.	Oxidizing Flame.			Reducing Flame.		
	Oxide.	Hot.	Cold.	Oxide.	Hot.	Cold.
Chromium,	Cr_2O_3	Yellow-red	Green	Cr_2O_3	Emerald green	Emerald green
Cobalt,	CoO	Blue	Blue	Co O	Blue	Blue
Copper,	Cu O	Green	Blue	Cu_2O	Colorless	Red (opaque)
Iron,	Fe_2O_3	Red	Yellow	Fe O	Bottle-green	Bottle-green
Manganese,	Mn_2O_3	Violet	Amethyst-red	MnO	Colorless (Faint rose)	Colorless (Faint rose)
Nickel,	Ni O	Violet	Red-brown	Ni	Gray (Turbid)	Gray (Turbid)
Uranium,	U O_3	Red-brown	Yellow	U_3O_8	Green	Green

Experiment IV.—Detection of Boron. Tests.

(*a*) Dissolve a small quantity of boric acid in 10 cm.^{3} of alcohol (ethyl or methyl). Pour a portion of the mixture into an inverted porcelain crucible cover and set fire to it, noting the color of the flame (?).

(*b*) To a strong aqueous solution of borax in a test tube provided with a cork carrying a glass jet, add a little sulphuric acid, then a volume of alcohol equal to that of the solution. Heat the mixture and inflame the vapor issuing from the jet (?). Equations?

(*c*) Dip the end of a platinum wire, successively, into concentrated H_2SO_4, glycerine, and powdered borax. Hold the wire in the outer edge near the bottom of a small Bunsen flame. What color is imparted to the flame?

(*d*) Reaction with turmeric. Dip a strip of turmeric paper into a solution of boric acid, or a borate to which has been added a little HCl or H_2SO_4 to liberate the boric acid. Observe the production upon the paper of a characteristic red-brown stain. The color is distinguished from that produced by the alkalies by the fact that when it is touched with a drop of an alkali solution, the brown color is changed to a greenish-black color, but is restored to its original color and is not discharged by dilute HCl or H_2SO_4.

The only borates which are readily soluble in water are those of the alkalies. Magnesium borate together with a few others are difficultly soluble.

The similarity of boron and aluminum may be inferred from the data incorporated in the appended table:

Physical Properties.	Boron.	Aluminum.
Atomic weight,	11.0	27.1
State or phase,	Solid (Amorp.—Cryst.)	Solid
Color,	Transparent (Cryst.)	Silver-white
Specific gravity,	2.5–2.63	2.58 (Hammered)
Specific heat,	<————————<	
Melting point,	Infusible	657°
Chemical Properties,		
H-derivatives,	BH_3	———
State or phase,	Gas	———
Halides,	BCl_3	$Al Cl_3$; Al_2Cl_6
Heat of formation,	104,000 cal.	321,900c al. (Al_2Cl_6)
State or phase,	Liquid	Solid
Stability,	Unstable in water	Stable in water
O-derivatives,	$B_2 O_3$	Al_2O_3
Heat of formation,	317,200 cal.	388,900 cal.(Al_2O_3, $3H_2O$)
State or phase,	Solid	Solid
Stability,	Soluble	Insoluble
Acids,	(H_3BO_3) ($H BO_2$) ($H_2B_4O_7$)	($H_3Al O_3$) ($H Al O_2$) ($H_2Al_2O_4$)
Stability,	Stable in water	Unknown in the free state.

CHAPTER XXIII.

THE METALS OR BASE-FORMING ELEMENTS.

Introductory Note.—On account of certain physical and chemical properties common to a large number of the elements, but wanting in a greater or lesser degree in others, the elements are, as suggested previously, grouped into *non-metals*, *metalloids*, and *metals*. In our previous work we have studied chiefly the *non-metallic* or *acid-forming* elements. We are now ready to begin the systematic study of the *metals*, having studied but one typical metal, namely, *sodium.*

The metals have already been defined as *base-forming* elements. They are usually good conductors of heat and electricity, and are endowed with a peculiar luster which is known as *metallic luster.* Although the number of metallic elements is much larger than that of the non-metals, the chemistry of the former is less diverse and more simple.

The student is again reminded that there is no sharp distinction between metals and non-metals, but rather a gradual merging of one class into the other, depending on whether the distinction is based upon their physical or chemical properties.

Physical Properties of the Metals.

1. At ordinary temperatures metals are *solids* with the exception of mercury.

2. The relatively high *conductivity* of the metals for *electricity* is characteristic.

3. The metals when in the compact form are endowed with a *metallic luster.* With the exception of copper and gold, the metals in compact masses possess a silver-white color. Most of the metals are black when in a powdered condition, magnesium and aluminum being notable exceptions.

4. Many of the metals possess the property of *tenacity* in a very considerable degree.

5. All of the metals can be obtained in the *crystallized* form.

6. The metals vary widely as regards *specific gravity* and *volatility* and *fusibility.* (See tables.) Those metals which have a sp. gr. less than 4 (5, and even 6, are sometimes given as the limit) are called the light metals, and those with a greater sp. gr., the heavy metals.

7. *Malleability* is a property peculiar to most of the metals. Antimony and bismuth are reduced to powder when hammered.

8. Many of the metals when in the molten condition dissolve in one another forming mixtures which are sometimes spoken of as *undetermined compounds*, but more often as *alloys.* These alloys frequently possess properties very similar to solid solutions. They are generally more

fusible than their component metals. "Wood's metal" is an alloy which melts at about 66° C., and contains bismuth 4 parts, lead 2 parts, tin and cadmium, each 1 part. (See Table of Alloys.) Alloys in which mercury is one of the components are known as *amalgams.*

Chemical Properties Characteristic of the Metals.

1. The oxides and hydroxides of the metals usually exhibit *basic* properties.
2. The metals manifest but *little tendency* to form combinations with hydrogen.
3. Each metal is able to function as a *positive radical* in a salt, and to exist as a *positive ion* in aqueous solutions of said salt.
4. The metals show a *strong attraction for the halogen group* of elements, forming compounds which as a rule are soluble in water but are not hydrolyzed.

There are numerous other chemical properties which are characteristic of metals, and which may serve as a basis of distinction between metals and non-metals, but they are not common to *all* the metals. The student will become familiar with these various properties as the work progresses.

Occurrence of the Metals in Nature.—Certain metals are found in nature free of all combination. When a metal cocurs thus it is said to be *native.* Platinum, gold, silver, copper, bismuth, arsenic, antimony, mercury, etc., are found in the native state. More often the metals are found in nature in combination with one or more of the other elements, as oxides, chlorides, sulphides, carbonates, sulphates, phosphates and silicates. When elements or compounds, or mixtures of elements or compounds, possessing definite physical properties, are found in nature, they are usually given the name of *minerals.* Various rocky materials known as the *matrix* usually accompany the minerals. The minerals, or the minerals and the rocks (matrix) in which they occur, are called *ores.* The art of extracting the metals from their ores is called *metallurgy.* The process of extracting the metals frequently consists of heating the ore with a *flux* which combines with the matrix and other undesirable portions, giving a fusible *slag.* The separation of the fused slag and the molten metal is easily effected.

The following outline states the forms in which the metals occur in the greatest abundance, and are of chief importance, commercially:

Native.
Gold
Platinum
Silver

Chlorides (chiefly).
Potassium
Sodium
Lithium

Carbonates.
Barium
Calcium
Copper
Iron
Lead
Magnesium
Manganese
Strontium

Silicates.
Aluminum
Calcium
Lithium
Magnesium
Potassium
Sodium

Oxides.
Aluminum
Copper
Chromium
Iron
Manganese
Tin
Zinc

Sulphides (chiefly).
Antimony
Arsenic
Cadmium
Cobalt
Lead
Mercury
Molybdenum
Nickel
Silver
Zinc

Sulphates.
Barium
Calcium
Lead
Strontium

Phosphates.
Calcium

Classification of the Metals.—There has been much discussion as to the best classification of the metals. The question cannot be answered categorically and it is well to remember that for purposes of study, the metals may be grouped variously, according to the selection of those properties which are made the basis of comparison. Valence alone may serve for classification, and in such case the arrangement will be very similar to that of the periodic system. Again, the scheme of classification may be based on the analytical behavior of the metals. This latter arrangement will bring together in many cases those metals belonging to one group of the periodic system, but in a few instances the elements of a periodic group are separated. It is evident, then, that any one scheme of classification must be one-sided as emphasizing certain similarities more strongly than others.

The following grouping has been suggested by Ostwald:

Non-metals.	Metals.	
Hydrogen and the halogens.	Alkali metals.	Light metals
The oxygen group.	Alkaline earth metals.	
The nitrogen group.	Earth metals.	
The carbon group.	The iron group.	Heavy metals
The argon group.	The copper group.	
	Other metals.	

In the work which follows the metals will be considered in the order in which they occur in families of the *periodic* grouping. This arrangement affords a general view of the metals as brought together in the natural groups of elements:

Elements of Group I:

Family M. (alkali metals).—Lithium, sodium potassium, rubidium, cæsium and the radical ammonium, NH_4, which is known as the "hypothetical" metal.

Family m.—Copper, silver and gold.

Elements of Group II:

Family M (alkaline earth metals).—Beryllium (glucinum), Magnesium, calcium, strontium, barium and radium.

Family m.—Zinc, cadmium and mercury.

Elements of Group III:

Family M (earth metals).—Scandium, yttrium, lanthanum, ytterbium.

Family m.—Boron, aluminum, gallium, indium, thallium.

Elements of Group IV:

Family M.—Titanium, zirconium, cerium, thorium.

Family m.—Carbon, silicon, germanium, tin, lead.

Elements of Group V:

Family M.—Vanadium, columbium, and tantalum.

Family m.—See Nitrogen Family.

Elements of Group VI:

Family M.—Chromium, molybdenum, tungsten and uranium.

Family m.—See Oxygen Family.

Elements of Group VII:

Family M.—Manganese.

Family m.—See Chlorine Family.

Transitional Elements:

Of the First Long Period.—Iron, cobalt and nickel.

Of the Second Long Period.—Ruthenium, rhodium and palladium.

Of the Fourth Long Period.—Osmium, iridium and platinum.

CHAPTER XXIV.

ALKALI METALS.

Lithium,	Li,	7.03
(Ammonium,	NH_4,)	
Sodium,	Na,	23.05
Potassium,	K,	39.15
Rubidium,	Rb,	85.5
Cæsium,	Cs,	132.9

The metals of this family, together with their corresponding compounds, bear a very close resemblance to one another. This family includes those metals which are chemically the most active. The activity increases with increased atomic weight. The metals tarnish very quickly when exposed to the air owing to rapid oxidation. They decompose water violently, liberating hydrogen. The oxides and hydroxides have strongly basic properties. Their salts with the "active" acids do not undergo hydrolysis when in aqueous solution. They are univalent, and are never found in anions.

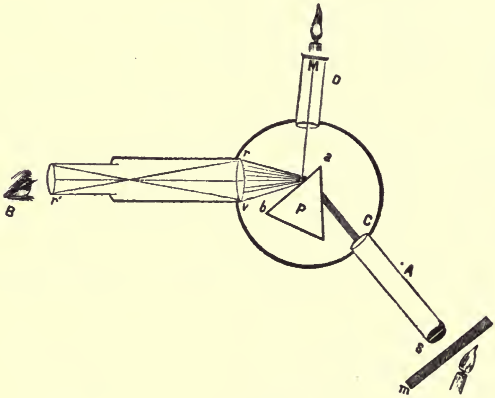


Fig. 46.

The compounds of ammonium will be discussed with those of potassium to which they show a marked similarity.

LITHIUM, Li.

At. Wt. 7.03 Sp. Gr. 0.59.

Experiment I.—Flame Color of Lithium Compounds.

Clean a platinum wire by alternately dipping it into hydrochloric acid and heating in the Bunsen flame until it gives apparently no color to the flame, then dip the wire into a dilute solution of lithium chloride and hold it in the Bunsen flame. Notice the color of the flame and examine it with the spectroscope (Figs. 46 and 47) (Instructions) (?). Make a diagram of the "scale" showing the relative positions of the sodium or D lines (yellow) and the lithium lines. Nearly all flames in the laboratory show the yellow lines owing to the presence of sodium.

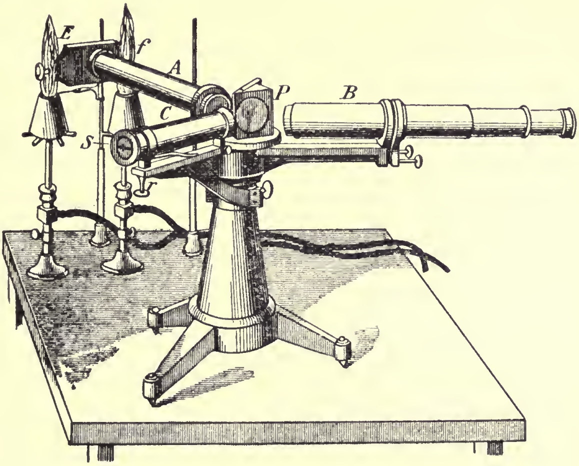


Fig. 47.—Single Prism Spectroscope.

All the common salts are readily soluble in water except the carbonate, phosphate and oxide which are soluble with difficulty.

SODIUM, Na.

At. Wt. 23.05 Sp. Gr. 0.97.

Experiment I.—Properties of Sodium.

(*a*) Recall from previous work, or repeat Exp. I., "Sodium." Read the accompanying note. (See "Acids, Bases and Salts.")

1. Tabulate its most obvious physical properties.
2. Is sodium harder or softer than most of the metals with which you are familiar?

3. Is it lighter or heavier than water?

4. Does sodium tarnish when exposed to the air? Explain.

5. Indicate by an equation the interaction of water and metallic sodium.

6. Enumerate the chemical and physical properties which indicate that sodium is a metal.

7. What is the flame color of sodium compounds?

(*b*) Examine at least ten different salts of sodium (end shelf), noting the obvious physical properties. Give the name, formula and color of each salt. Determine the solubility of these compounds. Tabulate the foregoing data.

Experiment II.—Preparation and Properties of Sodium Hydroxide.

(*a*) Dissolve about 25 grams of soda ash (Na_2CO_3) in 100 cm.^{3} to 125 cm.^{3} of water in a large beaker, and heat on a wire gauze to boiling. To 10 grams of fresh quicklime which has been powdered, add sufficient water to form a thin paste—"milk of lime." Use heat if necessary to start the slaking action. Add the milk of lime gradually, and with constant stirring to the boiling solution. (Why?) Continue to boil for several minutes (?), and stir constantly. Remove the flame, and allow the precipitate to settle. With a pipette or a small tube remove a little of the liquid to a test tube, and test for the presence of a carbonate; if found to be present add more milk of lime and boil; but if absent, decant the liquid into a bottle; cork, and allow it to stand until the suspended solid matter settles. Test a portion of the precipitate for the presence of a carbonate (?). Siphon off (or filter rapidly) the clear supernatant liquid by means of a glass siphon filled with water. A portion of the solution may be evaporated to dryness and the solid substance; the remaining portion should be preserved in a tightly-stoppered bottle (?).

(*b*) Take a little of the prepared solution between the fingers (?). Test it with litmus paper (?). Try the flame test (?). Add an excess of the solution to small quantities of very dilute solutions of each of the following substances in separate test tubes: ferrous sulphate (?); ferric chloride (?); zinc sulphate (?); mercuric chloride (?); copper sulphate (?). Boil the contents of the tube (?). Describe the color and structure* of each of the precipitates and state the affect of boiling same.

(*c*) Repeat (*b*), using the reagent labeled "NaOH Solution" (?). What is your inference as to the identity of the solution prepared in (*a*)? By what other names is sodium hydroxide known?

(*d*) Write equations representing the reactions involved in (*a*) and (*b*).

(*e*) Examine the sodium hydroxide (solid) as found on the side-shelf. (See instructor.) Expose a small piece to the air on a watch glass for several hours (?). Is it efflorescent or deliquescent?

(*f*) How can sodium hydroxide be converted into sodium chloride? Equation?

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* Gelatinous, flocculent, curdy, pulverulent, granular or crystalline.

Experiment III.—Purification of Sodium Chloride.

Note.—Common salt usually contains such impurities as calcium and magnesium chlorides, sodium sulphate, calcium sulphate, etc. The presence of the chlorides, magnesium and calcium, causes the salt to become moist, especially in damp weather.

Prepare a saturated solution of sodium chloride by grinding 50 grams of salt with 150 cm.^{3} of water in a mortar. Filter the solution into a beaker and conduct hydrogen chloride into it. It is suggested that this gas be prepared by placing a small handful of salt in a generating-flask, covering it with concentrated hydrochloric acid, and allowing concentrated sulphuric acid to drop slowly from a dropping-funnel into the mixture. The evolved gas is passed into the saturated salt solution by means of an inverted funnel or thistle tube which is attached to the delivery tube of the generator. The mouth of the funnel should dip just below the surface of the solution. Pure salt separates out as the operation continues, but the impurities remain in solution. (Why?) Explain the precipitation of the salt by hydrogen chloride. Indicate the action by means of "ionic" equations. When the precipitation has continued for sometime and considerable salt has separated, remove the generator, and allow the salt to settle, then decant the fluid and wash the salt with 15 or 20 cm.^{3} of cold water, and again decant. After this process of washing has been repeated several times, the last traces of water may be removed with a filter pump or by throwing the salt upon filter paper and pressing the salt with a spatula. Dry the salt by warming it in a porcelain dish while stirring constantly with a glass rod.

Describe the appearance of the purified salt. Preserve it in a small bottle for future use.

Experiment IV.—Preparation of Sodium Carbonate (Solvay Process).

To 80 cm.^{3} of water add 20 cm.^{3} of ammonium hydroxide. Using the foregoing mixture as a solvent, prepare a saturated solution of ammonium carbonate, then place the solution in a corked bottle and saturate it with sodium chloride. This can be done only by prolonged agitation with the powdered salt. Allow the suspended matter to settle, then decant the clear liquid into a bottle fitted with a cork and a delivery tube which reaches to the bottom; connect the delivery tube with the laboratory supply of carbon dioxide and saturate the solution with the gas. This latter operation may require nearly an hour. Finally filter off the precipitated matter, and dry the salt by pressing it between filter papers. Dissolve a little of the salt in a few cm.^{3} of water. Dip a clean platinum wire into the solution and hold it in the colorless Bunsen flame (?). Add hydrochloric acid to the solution and test the evolved gas for carbon dioxide (?). What are your conclusions as to the identity of the salt?

Experiment V.—Purification of Sodium Carbonate by Crystallization.

Using 100 grams of sodium carbonate, prepare a saturated solution of the salt at 32° C.; filter at the same temperature and collect the filtrate in a large porcelain dish; cool the solution to 0° C. by packing the dish in broken ice; heavy layers of white crystals soon form in the porcelain dish. Decant the supernatant liquid when the crystals are no longer deposited, then dry the crystals as thoroughly as possible by pressing them between layers of filter paper. Redissolve these crystals in water at 33° C. and repeat the foregoing process. The crystals are subjected to this treatment a third time, after which they are pressed and dried. The molecular formula of the salt is now $Na_2CO_3 . 10H_2O$. Place the crystals between watch glasses, and allow them to remain exposed to the air for several days. They effloresce, and in a comparatively short time are transformed into white powdery Na_2CO_3. Preserve the salt in a clean glass-stoppered bottle. The relative solubility of sodium carbonate at various temperatures is indicated in following table:

At 32°, 100 parts of water dissolve 1140 parts.
At 30°, 100 parts of water dissolve 273 parts.
At 20°, 100 parts of water dissolve 92 parts.
As 0°, 100 parts of water dissolve 21 parts.

Experiment VI.—Dehydration of Hydrous Sodium Carbonate.

Place about a gram of hydrated sodium carbonate in a test tube clamped so that its mouth is inclined slightly downward; heat tube to a dull redness, and note the change in the salt. What is evolved? Dissolve a small quantity of the anhydrous salt in a few cm.^{3} of water, and add a few drops of hydrochloric acid to the solution (?). Equations?

Experiment VII.—Action of Acids upon Sodium Carbonate.

Try the action of each of the following acids upon separate portions of a solution of sodium carbonate; hydrochloric acid (?); nitric acid(?); sulphuric acid (?); acetic acid (?). Represent the reactions by ionic equations.

Experiment VIII.—Hydrolysis of Sodium Carbonate.

Test a solution of purified sodium carbonate with litmus paper (?). Explain the reaction by the assistance of equations.

Experiment IX.—Preparation and Decomposition of Sodium Hydrogen Carbonate.

(*a*) Preparation. Make a saturated solution of sodium carbonate by warming (avoid boiling) it with water in a beaker; add an excess of the salt; allow the solution to cool, filter, and pass carbon dioxide into the filtrate until a precipitate forms (?). Indicate the reaction by an equation. Is sodium hydrogen carbonate more or less soluble than sodium carbonate? Test the solution with litmus paper and explain its reaction.

(*b*) Decomposition. Place about 1 gram of sodium hydrogen carbonate (bicarbonate of soda) in a test tube, add 10 cm.^{3} of water and heat gently. Test the evolved gas for carbon dioxide (?). Equations?

Experiment X.—Preparation of Sodium Hydrogen Sulphate.

Recall or repeat Exp. X. "Neutralization—Salts."

Experiment XI.—Reactions of Sodium Salts.

Note.—Use the purified sodium chloride for the following reactions.

(*a*) What color is imparted to the flame by sodium salts? Examine the sodium flame by means of a spectroscope. Locate its spectrum on the scale (?).

(*b*) To a few drops of a strong aqueous solution of the chloride on a watch glass add five or six drops of a platinic chloride, $PtCl_4$, solution. Evaporate *carefully* to small volume. Allow the mixture to cool, and determine the solubility of the red-colored monoclinic crystals (?), (a) in water, and (b) in alcohol (?).

(*c*) Sodium cobaltic nitrite, $Co(NO_2)_3 . 3NaNO_2$*, produces no precipitate in acetic acid solutions of sodium salts.

(*d*) Sodium salts are but slightly volatilized when heated in a porcelain dish over a Bunsen flame.

All sodium salts are soluble.

Experiment XII.—(Quant.) Alkalimetry and Acidimetry.

(*a*) Determination of the strength of a NaOH solution by titration. Calculate the weight of pure (99.95 per cent. purity) oxalic acid, $C_2H_2O_4 . 2H_2O$, required to make 500 cm.^{3} of a .5N oxalic acid solution. Powder and expose on a watch-glass for 20 min. a quantity of the acid slightly in excess of the calculated amount, then weigh out on glazed paper the exact amount. Transfer the oxalic acid to a 500 cm.^{3} graduated flask which has been previously calibrated, and fill the flask to the mark with distilled water. Fill a burette with the solution. Measure carefully into a small flask from another burette 10 cm.^{3} of the sodium hydroxide solution prepared in Exp. II, dilute† with twice its volume of water, and add a few drops of a phenolphthalein solution. Now cautiously run acid into the flask until the red color just disappears. Record the exact amount of acid used, and calculate (a) the weight of sodium hydroxide per liter, (b) the normality of the solution.

(*b*) If the sodium hydroxide solution is above normal, calculate the volume of water and solution necessary for the preparation of 100 cm.^{3} of a normal solution. If the solution is less than normal calculate the amounts required for 250 cm.^{3} of a half-normal solution of the alkali.

(*c*) Using the amounts calculated in (*b*) ,prepare either a normal or half-normal solution of the alkali.

(*d*) Using the solution prepared in (*c*), determine the normality of the

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* Sodium cobaltic nitrite may be prepared as follows: To 33 grams of sodium nitrite add 100 cm.^{3} of water, make slightly acid with acetic acid, then add 3.5 grams of cobalt nitrate. Allow the solution to stand for several hours, and filter if not clear. The solution decomposes slowly.

† A concentrated solution may decompose the indicator, phenolphthaleïn.

hydrochloric acid on the reagent shelf. Use methyl-orange (instructions) for an indicator.

How can the amount of acetic acid in vinegar be determined?

(*e*) Define alkalimetry. Acidimetry?

POTASSIUM, K.

At. Wt. 39.15 Sp. Gr. 0.87.

Experiment I.—Properties of Potassium.

(*a*) Observe the same caution in the manipulation of potassium as suggested in the use of sodium. Place a piece of potassium upon a dry paper and cut off a piece the size of a small pea. Observe the color and luster of the freshly cut surface (?). Note the effect of air (?). Why is it kept under kerosene? Is the potassium hard? Half fill a tall beaker with water which reacts neutrally. Scrape the coating from the piece of metal, and throw it (metal) upon the water contained in beaker which should be covered with a glass plate. Does the metal float? Is there any evidence of chemical action? Compare its interaction with water with that of sodium under similar conditions (?).

(*b*) Wrap a piece of potassium in a little paper; place it in a wire gauze basket; hold it under water and collect the gas which escapes in a test tube by displacement of water. Apply a lighted match to the mouth of the tube. Results? Identify the gas (?).

(*c*) Test the water in the beaker with red litmus paper (?). Take a little of the water between the fingers (?). Dip a clean platinum wire into the water and hold it in the colorless Bunsen flame. Is the flame colored? What is the color?

(*d*) Pour 3 $cm.^3$ of the shelf reagent labeled potassium hydroxide into a test tube and dilute with an equal volume of water. Repeat (*c*), using the foregoing solution. Results? Inference? Indicate the interaction of potassium and water by an equation. What is the valency of potassium?

(*e*) Place a drop of bromine in a porcelain dish and *cautiously* drop a fragment of potassium into it. Results? Equations?

(*f*) Put a small piece of potassium in a test tube with a little iodine. Result? Heat the tube gently. Results? Equation?

(*g*) Enumerate the chemical and physical properties which indicate that potassium is a metal.

Experiment II.—Potassium Salts.

Examine at least ten different salts of potassium, noting the obvious physical properties. Give the name, formula, color and solubility of each salt. Tabulate the foregoing data.

Experiment III.—Preparation and Properties of Potassium Hydroxide.

Proceed as in Exp. II, "Sodium." What are your conclusions as to the similarity of the chemical properties of sodium hydroxide and potassium hydroxide?

Experiment IV.—Action of Acids upon Potassium Hydroxide.

(*a*) Preparation of potassium sulphate. Dissolve 5 grams of potassium hydroxide in 20 cm.^{3} of water. Add two drops of a phenolphthalein solution, then neutralize the solution with dilute sulphuric acid. Evaporate until crystallization begins, then allow the solution to cool and note the formation of crystals. Equation?

(*b*) Preparation of potassium hydrogen sulphate. Prepare a solution of potassium hydroxide as in (*a*), neutralize with a measured quantity of dilute sulphuric acid, then add a volume of the dilute acid equal to that used in neutralizing the alkali. Evaporate to small bulk and cool. If a crystalline mass is not obtained, evaporate further and cool. Repeat if necessary. Equation?

(*c*) Repeat (*a*), using nitric instead of sulphuric acid. Equation?

(*d*) Repeat (*a*), substituting hydrochloric for sulphuric acid. Equation?

Experiment V.—Hydrolysis of Potassium Carbonate.

Repeat Exp. VIII, "Sodium," using potassium carbonate instead of sodium carbonate.

Experiment VI.—Preparation of Potassium Nitrate by Metathesis. Relative Solubilities of Sodium Chloride and Potassium Nitrate.

Dissolve 20 grams of sodium nitrate in 40 cm.^{3} of hot water. To the boiling solution add 18 grams of potassium chloride. Stir with a glass rod until all the salt is in solution. Evaporate to one-half this volume. What separates from the boiling mixture? Rapidly filter the mixture by decanting the hot clear liquid from the deposit of salt upon a filter. Set the filtrate aside to be examined later. Now throw the deposited salt upon the filter and press out the mother liquor with a spatula. Recrystallize this salt. Compare these crystals with any that may have formed in the filtrate from the original solution. Identify the two kinds of crystals (?).

The process may be understood more clearly by inspecting the solubilities of sodium chloride and potassium nitrate, the products of the interaction of the factors. The following table gives the number of grams dissolved by 100 cm.^{3} of water:

	At 0° C.	10° C.	100° C.
Sodium chloride,	35.6 grm.	35.63 grm.	39.9 grm.
Potassium nitrate,	13.3 grm.	25.00 grm.	247.0 grm.

Experiment VII.—Deflagration. Gunpowder.

(*a*) Pulverize separately and mix intimately 3 grams of potassium nitrate and 1 gram of sulphur. Throw the mixture into a red-hot iron crucible or ignite it on an iron plate. Results? Dissolve the residue in water. Devise a method for testing for potassium sulphate (?).

(*b*) Repeat (*a*), using powdered charcoal instead of sulphur. Test the residue for potassium carbonate (?).

(*c*) Powder separately and mix thoroughly on paper 6 grams of potassium nitrate, 1 gram of sulphur and 1 gram of charcoal. Place the mixture on an iron plate or brick in the hood and ignite it. What is gunpowder? Define deflagration.

Experiment VIII.—Preparation of Potassium Cyanide and Potassium Thiocyanate.

See Exp. XVI, "Carbon."

Experiment IX.—Reactions of Potassium Salts.

Note.—Use chemically pure potassium chloride for the following reactions:

(*a*) What color is imparted to the flame by potassium salts? Examine the potassium flame by means of a spectroscope. Locate its spectrum on the scale with reference to the sodium or D lines. Make a diagram.

(*b*) To a few drops of a strong aqueous solution of the chloride on a watch glass add three or four drops of a solution of platinic chloride, $PtCl_4$. Results? Equation? Determine the solubility* of the yellow crystalline precipitate (a) in water and (b) in alcohol.

(*c*) Sodium cobaltic nitrite, when added to concentrated solutions of potassium salts which contain acetic acid but no free inorganic acid, gives a yellow pulverulent precipitate. Equation?

(*d*) Potassium salts are but slightly volatilized when heated in a porcelain dish over a Bunsen flame.

Most potassium salts are soluble in water.

AMMONIUM, NH_4.

Experiment I.—Preparation and Properties of Ammonium Hydroxide.

Recall Exp. II, "Nitrogen." Repeat Exp. II, (*b*), "Sodium." Recall or determine the relative electrical conductivities of normal solutions of potassium hydroxide, sodium hydroxide and ammonium hydroxide. (See table, Degree of Ionization.) What ions do they possess in common? What are your conclusions as to the relative *activities* of these three bases? Would you class ammonium hydroxide among the *active* bases? Why? Can ammonium be obtained in a free state? In what state or condition does it exist? What name is frequently applied to it? Why?

Experiment II.—Preparation of Ammonium Salts.

Recall Exp. IV, "Nitrogen."

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* Potassium chloro-platinate (potassium platinic chloride) is soluble in 110 parts of water at 10° C.; nearly insoluble in alcohol, and quite insoluble in a mixture of alcohol and ether.

Experiment III.— Hydrolysis of Ammonium Chloride.

Test a solution of ammonium chloride with litmus paper. Explain result. Equation? What is *sal ammoniac?*

Experiment IV.—(Optional.) Preparation of the Unstable Ammonium Amalgam.

Place about 50 cm.³ of a saturated solution of ammonium chloride in a dish and warm gently. Remove the flame and add a small quantity of sodium amalgam (see Appendix) to the solution while warm. Results? Hold a piece of red litmus paper over the dish (?). Equation?

$$Hg_x.Na + NH_4Cl \rightarrow Hg_x.NH_4 + NaCl.$$
$$2Hg_x.NH_4 \rightarrow 2Hg_x + 2\overline{NH_3} + \overline{H_2}.$$

Experiment V.—Properties of Ammonium Salts.

(*a*) Dissociation. In a small dry evaporating dish heat successively small quantities of the chloride, the nitrate and the sulphate. Note the odor of the fumes. What is the common result? Explain the formation of the white cloud which appears above the heated salt. Is the reaction reversible? (Recall Exp. III, "Chemical Equilibrium.") Equation?

(*b*) Decomposition. Heat a small quantity of ammonium phosphate in a hard glass tube (?). Dissolve the residue in water and test with litmus paper. Results? Conclusions? Equation? Are all ammonium salts completely volatilized by simple heating? Is ammonia liberated from all salts of ammonium when they are heated? (Recall Exp. I, "Nitrogen and the Atmosphere," and Exp. XI, (*a*), "Nitrogen," before answering this last question.)

(*c*) Purification of ammonium chloride. Plug the stem of a large glass funnel with clean cotton-wool and invert it over the dish in which a mixture of sand and ammonium chloride is being heated. Continue to heat the salt until a heavy white layer of it accumulates on the inside of the funnel. Scrape the salt on to a piece of glazed paper and examine it. How does it compare in purity with the original mixture? Bottle the salt and save for use in Exp. VI.

Exp. VI.—Reactions of Ammonium Salts.

(*a*) Do ammonium salts impart color to the flame?

(*b*) Place a small quantity of an ammonium salt solution in a beaker or a flask and add a few cm.³ of a solution of sodium hydroxide or potassium hydroxide. Cover the beaker with a watch glass on the under side of which is placed a moistened piece of turmeric paper or red litmus paper. Heat the beaker gently. Result. Equation?

(*c*) To a few drops of a strong aqueous solution of the chloride on a watch glass add three or four drops of a solution of platinic chloride. Result? Equation? Determine the solubility of the yellow crystalline precipitate (a) in water and (b) in alcohol.

This yellow precipitate may be distinguished from the similar potassium salt by the fact that when heated strongly it leaves a residue of spongy platinum.

(*d*) Sodium cobaltic nitrite precipitates from acetic solutions of ammonium salts a yellow pulverulent precipitate. Equation?

(*e*) Nessler's solution (a solution of potassium mercuric iodide in potash) is used to detect small traces of ammonia in natural waters. It gives a brown precipitate, or imparts a color according to the quantity of ammonia present.

$$2(HgI_2,2KI) + 3KOH + NH_3 \rightarrow NHg''_2I,H_2O + 7KI + 2H_2O.$$

(*f*) Ammonium salts undergo dissociation or are decomposed when heated in a porcelain dish.

All ammonium salts are soluble in water. Reagents can form precipitations only in concentrated solutions.

Experiment VII.—Detection of the Alkali Metals in a Mixture.

How can the salts of sodium and potassium be distinguished from ammonium salts without the use of the flame and the spectroscope? How could you distinguish between the salts of sodium and potassium without the aid of the flame test or spectroscope? Devise a system of tests which will provide for the detection of the three alkali metals in a solution containing their respective salts. Apply the system to a "known" solution of their salts. Ask the assistant to give you an "unknown" solution. Test for the presence of the alkali metals. Report (?). Make a complete record of all work.

RUBIDIUM, Rb.

At. Wt. 85.5 Sp. Gr. 1.52.
See text-book and lecture notes.

CÆSIUM, CS.

At. Wt. 132.9 Sp. Gr. 1.88
See text-book and lecture notes.

Lithium, rubidium, and cæsium are usually placed in the category of *rare* metals. Lithium salts cost about 10 s. per pound while rubidium and cæsium salts can be obtained for £ 64 per pound.

PROBLEMS.

1. Calculate the percentage of sodium sulphate in Glauber's salt, $Na_2SO_4 \cdot 10H_2O$.

2. What weight of sodium carbonate is theoretically required to prepare 100 grams of sodium hydroxide?

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3.$$

3. How much *sal soda* (washing soda), $Na_2CO_3 . 10H_2O$, can be made from 1 kg. of sodium chloride? The equations are:

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl.$$
$$Na_2SO_4 + CaCO_3 + C \rightarrow Na_2CO_3 + CaS + 4CO.$$

4. How much potassium carbonate is necessary to prepare 100 grams of potassium hydroxide?

5. How many grams of sodium hydroxide are necessary to liberate the ammonia from 50 grams of ammonium nitrate? From 50 grams of ammonium sulphate?

CHAPTER XXV.

Copper, Cu. 63.6
Silver, Ag. 107.93
Gold, Au. 197.2

The elements of this family occur free in nature, and on this account are among those metals which were earliest known. They are used very extensively for ornamental purposes, and almost universally for coinage.

These metals present many additional properties which are in marked contrast to those of the alkali elements. They are among the least active metals. They do not interact with oxygen or water at ordinary temperature. **Silver** and **gold,** together with the platinum family, are known as the "noble metals" because of their greater resistance to the chemical influences of air and water and their easy recovery from combination by means of heat. The oxides and hydroxides, with the exception of silver oxide, Ag_2O, possess weakly basic properties. The halides of these metals, save those of silver, are hydrolyzed.

Upon the basis of the periodic classification these three elements fall into the same family, but in many of their chemical relations they are very dissimilar. For example, silver is uniformly univalent, forming one series of salts; **copper** is both univalent and bivalent, forming two series; gold is univalent and trivalent, and likewise forms two series. Univalent copper and gold bear a marked resemblance to mercury, but bivalent copper resembles manganese (Mn''), zinc (Zn''), iron (Fe'') and nickel (Ni''), and trivalent gold bears a resemblance to aluminum (Al''') and iron (Fe'''). On the other hand, silver chloride, AgCl, and cuprous chloride, Cu_2Cl_2, are both soluble in ammonia but insoluble in water.

It is quite obvious that that family is not homogeneous, yet in many of their physical attributes these metals show a regular gradation in their properties. As regards ductility and malleability, silver is intermediate between copper and gold, the latter possessing these properties in the maximum degree. With respect to tenacity, silver is also intermediate, gold being the least tenacious of the three metals. These metals are the three best conductors of electricity. The electrical conductivity of silver exceeds that of all other metals.

COPPER, CU.

At. Wt. 63.6 Sp. Gr. 8.95.

Experiment I.—Properties of Copper.

(*a*) Procure a piece of copper wire, and clean the surface by scraping it with the blade of an old pen-knife or by scouring it with sand. Observe and state its most obvious physical properties. Is copper a good conductor of electricity? Of heat?

(*b*) Oxidation of copper. Repeat or recall Exp. XVII, (*e*), "Carbon." Equation? What change is slowly undergone by copper when exposed to the air? Upon what experimental evidence is your answer based?

(*c*) Solution tension. Place 5 cm.^{3} of a solution of any compound of mercury in a test tube, then dip a clean copper wire into the solution. After a short time, remove the wire and rub it carefully with a soft cloth. Result? Has any of the copper passed into solution? Explain. Equation? Compare the action with that which takes place when zinc acts upon sulphuric acid.

Insert an iron nail or wire and a strip of zinc into separate test tubes half-filled with a copper sulphate solution. After a short time remove the metals and examine them. Result? Has the color of the copper sulphate solution undergone any change? Account for results? Equations?

(*d*) Solubility in acids. Using small portions of copper filings in separate test tubes, determine the solubility of the metal in hydrochloric acid. In nitric acid diluted with half its volume of water? In strong sulphuric acid? In *aqua* regia? Use heat, if necessary, in each case? Equations? What color is common to the various solutions? Recall Exp. IV, (*b*), (*c*). "The Modern Theory of Solution." How does the electrolytic dissociation theory account for the similarity in color of the solutions enumerated?

(*e*) Make a list of the *alloys* of which copper is one of the components. (See Appendix.)

Experiment II.—Reduction of Cupric Oxide.

(*a*) Recall Exp. VIII, "Hydrogen." Equation?

(*b*) Thoroughly mix on paper about 2 grams of cupric oxide and 0.1 gram of powdered charcoal; place the mixture in a test tube and heat. Test the evolved gas for oxygen and carbon dioxide, and examine the residue in the tube. Results? Equation?

Experiment III.—Preparation and Properties of Cuprous Oxide.

To 10 cm.^{3} of Fehling's solution in a test tube add 4 or 5 cm.^{3} of a dilute solution of glucose, or a solution of cane sugar which has been boiled with a few drops of hydrochloric acid for 10 minutes. (?). Boil the mixture* vigorously for several minutes. The red precipitate is cuprous oxide. Explain its formation.

Divide the precipitate into three parts. Expose one portion to the action of the air (?). To the second portion add strong nitric acid and boil (?). Equation? Add ammonium hydroxide to the third portion, and shake the solution in a test tube. Result?

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* The solution must be strongly alkaline.

Experiment IV.—Preparation and Properties of Cupric Hydroxide. Cupric Oxide.

To 3 cm.^{3} of a solution of copper sulphate add an excess of a solution of sodium hydroxide. Results? Write the reaction. Boil one-half the mixture and account for the change in the color of the precipitate. Equation? To the other half of the mixture add ammonium hydroxide. Result? Equation? Write the formula of the complex ion which imparts the deep blue color to this solution.

Experiment V.—Ammonio-cupric Compounds, Cuprammonium. Ammonio-cuprous Compounds, Cuprosammonium.

(*a*) Add ammonium hydroxide, at first in small amounts, then in excess, to a solution of cupric sulphate. Results? Give the formula for ammonio-cupric sulphate. The copper now forms a part of what ion? Equations? Would you infer that the concentration of the cupric ion in the latter solution is greater or less than in the copper sulphate solution?

(*b*) Place 10 or 15 cm.^{3} of a cuprammonium sulphate solution in a large test tube, add an excess of copper filings or turnings, cork air-tight, and set aside until the solution has become colorless. Account for the change in color of the solution by use of an equation. What is the formula of the colorless complex ion? Now remove the cork from the tube and shake the solution with air. Results? Equation?

Experiment VI.—Preparation and Degree of Hydration of Cupric Chloride.

(*a*) Recall Exp. I, (*d*). Indicate the interaction of copper and hydrochloric acid by an equation.

(*b*) Put 2 to 3 grams of cupric oxide in a test tube or small flask, add a little hydrochloric acid which has been diluted with an equal volume of water, boil, and continue to add acid until all of the copper oxide is dissolved. What is the color of the solution? Equation?

Place three-fourths of the solution in an evaporating dish, evaporate, and crystallize. State color and formula of crystals. To one-half of the remaining solution add water slowly and observe the color (?). To the other portion add concentrated hydrochloric acid and observe the color. Account for any change of color. Equations? What is the color of anhydrous cupric chloride?

(*c*) Write the formulæ for the following salts of copper: Verdigris, blue vitriol, paris green, cupric nitrate, Scheele's green, copper acetate.

Experiment VII.—Formation and Behavior of Cuprous Chloride.

(*a*) To 3 grams of cupric chloride dissolved in 15 cm.^{3} of water in a small flask, add 5 cm.^{3} of concentrated hydrochloric acid and about 7 grams of copper filings or turnings; an excess of copper must be used. Boil the mixture until it is colorless, or a drop of the brownish-black liquid gives a white precipitate when added to a test tube full of water.

Pour the liquid into a large volume of water in a beaker. Wash the white precipitate by decantation, and keep it under water until used. What change have the cupric ions undergone? Equation?

(*b*) Expose a little of the cuprous chloride covered with water, in a test tube, to the sunlight. Result? The reaction is said to be represented by the following equation:

$$2\mathrm{Cu\,Cl} \longrightarrow \mathrm{CuCl_2} + \mathrm{Cu}.$$

(*c*) Cuprous chloride dissolves in concentrated hydrochloric acid giving the two colorless complex acids, $HCuCl_2$ and H_2CuCl_3. Equations? What is the complex anion formed as the result of the above reaction? Do complex ions tend to dissociate? Show by ionic equations the various equilibria involved in a solution* of cuprous chloride in hydrochloric acid.

(*d*) To a hydrochloric solution of cuprous chloride add a little concentrated nitric acid. The resulting color of the solution shows what ion to be present? Explain.

Define oxidation in terms of the electrolytic dissociation theory.

(*e*) Cuprous chloride is soluble in ammonium hydroxide giving a colorless solution which quickly turns to a deep-blue owing to the oxidizing action of the air. Equations?

(*f*) Precipitation of hydrated cuprous oxide. Add an excess of a sodium hydroxide solution to a hydrochloric acid solution of cuprous chloride. Result? Equation? Divide the mixture into two portions. Boil one portion. Result? Equation? Shake the other portion with air in a test tube. Result? Equation?

Experiment VIII.—Precipitation of Cuprous Iodide.

Add a small quantity of a solution of potassium iodide to 10 cm.³ of a very dilute solution of cupric sulphate. Observe the color of the solution and the precipitate (?). Filter and wash the precipitate. Divide the filtrate into two parts. Add one part to a dilute cold starch emulsion (?). Shake the other part with a little chloroform or ether (?). Equations?

Experiment IX.—Dehydration of Hydrated Cupric Sulphate.

See Exp. VIII, (*a*), "Water." Powder a small crystal of cupric sulphate, and dehydrate it by heating it gently in a test tube clamped in a nearly horizontal position. Results? Equation? What is the effect of a little water upon the anhydrous salt?

Experiment X.—Decomposition of Cupric Nitrate. Preparation of Pure Cupric Oxide.

Dissolve 5 grams of cupric nitrate in 25 cm.³ of distilled water, filter off any insoluble particles, evaporate the filtrate to dryness in the hood,

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* The solution of cuprous chloride in hydrochloric acid or ammonium hydroxide is a valuable reagent used in gas analysis for the absorption of carbon monoxide.

and heat the dry residue in a porcelain crucible until it is of a uniform black color. Equation?

Experiment XI.—Precipitation of Basic Cupric Carbonate.

To a solution of cupric sulphate add a slight excess of a sodium carbonate solution (?). Explain the participation of water in this reaction. Boil the mixture with an excess of the precipitant (?). Equation? What is *malachite*? Its formula?

$$2CuSO_4 + 2Na_2CO_3 + H_2O \rightleftarrows Cu_2(OH)_2\underline{CO_3} + Na_2\underline{SO_4} + \overline{CO_2}.$$
$$2Cu_2(OH)_2CO_3 \rightleftarrows Cu_4O_3(OH)_2 + CO_2 + H_2O.$$

Experiment XII.—Precipitation of Cupric Ferrocyanide.

Add a solution of a potassium ferrocyanide to a very dilute solution of cupric sulphate. Result? Equation?

Experiment XIII.—Preparation of a Double Salt. Potassium-Cupric Sulphate.

Using 5 grams of powdered cupric sulphate, prepare a saturated solution at 70°. Calculate the weight of powdered potassium sulphate which must be taken to give the same fraction of its molecular weight. Dissolve this weight of salt in its own weight of water at 70°, and add a few drops of sulphuric acid. Mix the two solutions, taking care to secure complete solution of both salts before mixing. Pour the mixture into a beaker or crystallizing dish and set it aside to crystallize. Examine the whitish-blue crystals and compare them with those of cupric sulphate (?). Give the molecular formula of the crystals. Dry the crystals between layers of filter paper and preserve them in a stoppered bottle for future use.

Dissolve a part of the crystals in water. Is the cupric ion present in the solution? By what experimental evidence can you support your answer?

Do "compound salts" yield complex ions?

Experiment XIV.—(Quant). Equivalent of Copper.

Dissolve an accurately weighed amount (about 2 grams) of cupric sulphate in distilled water in a beaker. Record the weight. Procure a small rod or bar of pure zinc, file and scour it until its surface is smooth and clean; wash and dry it, then weigh accurately. Record the weight. Place the zinc in the solution and allow it to remain there until the latter becomes colorless. Take the zinc out of the solution, carefully remove the brown deposit (?) by directing a small stream of water against it; dry and weigh it. Record the weight. What weight of zinc has gone into solution? Assuming that all of the copper has been displaced from the solution, calculate from the formula the weight of copper deposited upon the zinc. This weight of copper will be the *equivalent* of the weight of zinc in solution.

The atomic weight of zinc is 65.4. Calculate the atomic weight of copper from above data.

Experiment XV.—(Quant.) Determination of the Percentage of Copper in Cupric Sulphate Crystals by Electrolysis.

Dissolve an accurately weighed amount of pure cupric sulphate in water in a weighed platinum crucible or dish. Use 10 cm.^{3} of water for each .1 gram of salt. Add 10 drops of concentrated nitric acid to make the solution thoroughly acid, and to prevent the copper from depositing in a loose, spongy form instead of a hard, smooth plate. Cover the crucible with a perforated watch glass, and suspend a flat spiral of platinum in the solution. Place the crucible on an electrolysis stand. (Instructions.) Connect the stand with the source of electricity (a battery of four to eight gravity cells may be used) in such a manner that the platinum spiral becomes the anode and the crucible the cathode. The *density* (ND_{100}) of the current should not be greater than 1 ampère, nor should the electrode tension exceed 2.5 volts. As the current continues to act, observe the changes which occur in the crucible (?). To determine when the deposition of the copper is complete, a drop of the liquid is taken out from time to time after about five hours, and tested on a porcelain surface with a drop of potassium ferrocyanide which has been acidified with hydrochloric acid. When the electrolysis is finished, the crucible is removed, carefully and repeatedly washed with water and then with small quantities of alcohol, and dried in an air bath at 90° C. Desiccate and weigh. What is the weight of the copper deposited? Calculate the percentage of copper by weight in cupric sulphate crystals. Compare with that calculated from the molecular formula.

Explain electro-plating in terms of the electrolytic dissociation theory.

Experiment XVI.—Analytical Reactions of Cupric Salts.

(*a*) Dip a platinum loop into a solution of any cupric salt and hold it in the Bunsen flame. The compound imparts to the flame a brilliant blue color which instantly changes to green when the supply of acid is exhausted.

(*b*) Mix a small quantity of any cupric salt with sodium carbonate and heat strongly upon charcoal in the reducing flame (?). Equation?

(*c*) The borax bead test. Copper compounds give what color to it (a) when heated in the oxidizing flame; (b) in the reducing flame? Observe in each case whether the color of the bead while hot is identical with that when the bead is cold.

(*d*) Prepare a dilute solution of pure cupric sulphate and test the reaction of the solution with litmus paper (?). Explain the result.

Do the salts of active metals undergo hydrolysis? What is your inference as to the chemical activity of copper as a metallic element?

(*e*) Pass hydrogen sulphide through 5 cm.^{3} of a dilute solution of cupric sulphate (?). Filter and divide the precipitate into three parts.

Determine the solubility of cupric sulphide in sulphuric acid (?).

Write the reaction for the precipitation of cupric sulphide from cupric sulphate with hydrogen sulphide. Is the reaction reversible? Upon what experimental evidence do you base your answer?

Ascertain if cupric sulphide is soluble in (a) nitric acid (?), (b) yellow ammonium sulphide (?). Equations?

(*f*) To a dilute solution of cupric sulphate add a potassium cyanide solution (poison) drop by drop. Observe the precipitation of the unstable cupric cyanide, which readily decomposes into cyanogen and cuprous cyanide. Equations?

Is cuprous cyanide soluble in an excess of potassium cyanide? Does the resulting solution show the color of the cupric ion? Is the cupric ion present? If not, of what ion does the copper now form a part? What general name is given to this class of ions? Equation?

Pass hydrogen sulphide through a solution of cupric sulphate which has been decolorized by the addition of an excess of potassium cyanide (?). Do results indicate the absence or presence of the cupric ion? Explain.

(*g*) The deep-blue color imparted to solutions containing copper salts by the addition of an excess of ammonium hydroxide, and the deposition of copper upon strips of iron or zinc when immersed in solutions of salts of the former are tests frequently used. Equations?

Experiment XVII.—Experimental Study of Compound Salts and Complex Salts.

Using the crystals preserved from Exp. XIII, prepare a solution of potassium-cupric sulphate. Is this a double salt or a complex salt? Is the cupric ion present in the solution? Give a reason for your answer. Pass hydrogen sulphide through the solution (?). Do the results support your previous conclusion as to the presence of the cupric ion? Explain.

Recall or repeat Exp. XVI, (*f*).

Explain in terms of the ionic hypothesis the difference between "double salts" and "complex salts."

The scheme of ionization for "double salts" is identical with that of "complex salts."

Double salt, $K_2SO_4.CuSO_4.6H_2O$:

$$K_2Cu(SO_4)_2 \rightleftarrows 2K^{\cdot} + Cu(SO_4)''_2 \qquad (I)$$

$$Cu(SO_4)''_2 \rightleftarrows CuSO_4 + SO''_4 \qquad (II)$$

$$Cu(SO_4) \rightleftarrows Cu^{\cdot\cdot} + SO''_4 \qquad (III)$$

Complex salt,

$$K_4Fe(CN)_6 \rightleftarrows 4K^{\cdot} + Fe(CN)'''' \qquad (I')$$

$$Fe(CN)''''_6 \rightleftarrows Fe(CN)_2 + 4CN' \qquad (II')$$

$$Fe(CN)_2 \rightleftarrows Fe^{\cdot\cdot} + 2CN' \qquad (III')$$

The ionization corresponding to equations (II) and (III) are practically complete for double salts at infinite dilution, and for complex salts under similar conditions the reactions corresponding to equations (II′) and (III′) take place only to a very limited extent; in fact, so small, that our ordinary chemical tests fail to indicate the presence of the Fe'' ion.

The results of refined measurements indicate that simple ions exist to a very small extent in dilute solutions of complex salts and that complex ions are found in solutions of double salts, except at great dilution. It is obvious that the distinction between "double" and "complex" salts is one of degree and not of kind.

SILVER, Ag.

At. Wt. 107.93 Sp. Gr. 10.5.

Experiment I.—Properties of Silver. Preparation of Silver Nitrate.

(*a*) Examine a small piece of silver and make a record of the most obvious physical properties of the metal.

Does silver undergo oxidation when exposed to the air? Upon what observation do you base your answer?

(*b*) Dissolve a small piece of silver in nitric acid diluted with an equal volume of water (?). Evaporate the solution to small bulk and crystallize. Dry the crystals and place them in a bottle. Use these crystals for preparing solutions of silver nitrate. Indicate the interaction of nitric acid and silver by means of an equation.

Experiment II.—Electrolytic Deposition of Silver. "Silver Tree."

Dissolve about 15 grams of silver nitrate in 40 cm.^{3} of water. Place the solution in a small glass beaker or crystallizing dish. Introduce platinum electrodes into the solution so that they will be diametrically opposite to one another. Join these electrodes to the battery wires. Allow the action to continue for 30 minutes or longer. A beautiful deposit of silver will be made on the cathode. This deposit which spreads from the cathode toward the anode is called the "silver tree" because of its strong resemblance to vegetable growth.

Experiment III.—Replacement of Silver in its Compounds by Copper.

Place a strip of iron, zinc, tin, lead or copper in a solution of silver nitrate contained in a test tube. Result? Ionic equation? Examine the table of "Solution Tensions." Name the above metals in the order of increasing solution tension. Does silver ordinarily displace hydrogen from aqueous solutions of the acids?

Experiment IV.—Precipitation of Silver Oxide.

To a dilute solution of silver nitrate add a sodium hydroxide solution? Result? Equations? Is the precipitate soluble in excess of the precipitant?

Experiment V.—Preparation and Behavoir of the Halides of Silver.

(*a*) Silver chloride. To 5 cm.^{3} of a dilute solution of silver nitrate add a slight excess of dilute hydrochloric acid (?). Equation? Filter and wash the precipitate with water.

Put a small part of the precipitate upon a watch glass and expose it to direct sunlight (?). Equation?

To a second portion of the precipitate add ammonium hydroxide (?). Equation? What complex ion is formed? Now add dilute nitric acid drop by drop in excess (?). Equation?

Treat the third portion of the precipitate as in the preceding case, using an ammonium carbonate solution instead of ammonium hydroxide. Equations?

(*b*) Silver bromide. Repeat (*a*), substituting a potassium bromide solution for the hydrochloric acid.

(*c*) Silver iodide. Repeat (*a*), using a solution of potassium iodide in place of the hydrochloric acid.

What extensive practical use is made of the change produced in silver salts by light? Do the halides of silver show any gradation as to color? If so state it?

Experiment VI.—Preparation of Pure Silver from an Alloy.

Dissolve a copper-silver alloy in dilute nitric acid in a beaker or casserole. Use heat if necessary. Does the solution possess any property which indicates the presence of copper? Explain. Evaporate just to dryness, and take up the residue with warm water. Filter, add a few drops of nitric acid to the filtrate, and while stirring add dilute hydrochloric acid in slight excess. Continue to stir the mixture until the major portion of the precipitate has collected together. Filter and wash with water containing a few drops of nitric acid. Place the precipitate in a beaker, put several pieces of granulated zinc on it, and add sufficient dilute sulphuric acid to cover contents. The mixture should be stirred from time to time. Equation?

After several hours, pour off the acid, remove any unchanged zinc, wash the precipitate with water by decantation, and filter. Dry the brown powder between sheets of filter paper, then fuse it on a stick of charcoal by directing the flame of a blast-lamp downward upon it (?). Scour the metal bead with sea sand (?).

What is *sterling silver*? What is the composition of *standard* silver coin?

Experiment VII.—Precipitation of Silver Sulphide.

(*a*) Pass hydrogen sulphide through 2 or 3 $cm.^3$ of a dilute solution of silver nitrate (?). Equation? Is this reaction reversible theoretically? To a portion of the product add dilute nitric acid. What are your conclusions now as to the reversibility of the above reaction?

(*b*) Expose a silver coin to the action of hydrogen sulphide (?). What happens chemically when silver spoons are used to "beat" an egg? What is "oxidized silver"?

Silver is "tarnished" by the sulphur in perspiration.

Experiment VIII.—Action of Sodium Thiosulphate upon Silver Salts.

Treat small quantities of each of the following substances with a strong cold solution of sodium thiosulphate; silver chloride, silver bromide and silver sulphide (?). Equations? Other insoluble salts of silver behave in a similar manner.

Sodium thiosulphate ("hyposulphite of soda" or "hypo") is used largely in photographic processes for *fixing* the image; i.e., for dissolving out the unreduced silver halide on the photographic plate.

Experiment IX.—Photography.

Dip a piece of unsized paper (a filter paper will do) in a sodium chloride solution; allow the paper to drip for a few seconds, then dip it in a dilute solution of silver nitrate. Place an opaque object upon the paper and expose to the light until the paper around the object has a deep purple color, then dip it successively into a solution of potassium-ferrous oxalate* (a mixture of solutions of ferrous sulphate and potassium oxalate), distilled water, a solution of sodium thiosulphate and distilled water. Dry the paper and fasten it in your laboratory note-book. The foregoing procedure is similar in principle to that involved in the preparation of a "negative" of a picture. Explain the chemistry of each step in the procedure. Equations?

Photography involves two processes—the preparation of the "negative" and the printing of the "positive." The *negative* of a picture is usually taken upon a prepared plate of glass, and from this the positive is printed upon sensitized paper. The negative shows the "lights and shades" reversed, hence the name. The positive gives the objects their true appearance, i.e., it is the *positive* of the original object.

The modern photographic plate usually consists of a glass plate covered with a gelatin emulsion in which is suspended finely divided silver bromide. This plate is exposed in a camera to the light from the object to be photographed. The silver salt is in part decomposed, the degree of decomposition being proportional to the intensity of the light and the duration of the exposure. Thus a dark object will reflect few light rays, and that part of the plate exposed to these rays will be but little affected. A white surface will act in a reverse manner.

According to one view, the exposure reduces certain portions of the silver bromide to a sub-bromide, perhaps Ag_2Br, as indicated by the following equations:

$$2\,AgBr \longrightarrow Ag_2Br + Br.$$

After exposure, there is usually little or no visible alteration in the film of the plate as the decomposition is only partial. The image must be *developed*. This is done by washing the plate with a reducing agent,

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* A sodium carbonate solution of pyrogallol is frequently used as the "developer" instead of the potassium-ferrous oxalate.

such as an alkaline solution of pyrogallol (photographer's "pyro") or a solution of potassium-ferrous oxalate. This solution, which is known as the developer, continues the action initiated by the light. The partly decomposed silver salt is affected *first*, and with a speed proportional to the intensity of the illumination undergone by each part. Some of the salt is reduced to *metallic silver:*

$$3Ag_2Br + 3FeC_2O_4 \rightarrow Fe_2(C_2O_4)_3 + FeBr_3 + Ag.$$

The *depth* of the silver deposit is thus proportional to the intensity of the light upon the original plate. Those portions which have received the most light have the larger amount of the silver salts decomposed and are dark in color.

It should be remembered that although the developer acts first upon those parts reached by light, it can reduce the whole of the halide upon the plate. When the relative intensities of the light effects—i.e., the "contrast" between the parts variously illuminated—have been brought out sufficiently, the plate is removed from the reducing solution. If allowed to remain in the developer long enough, all the silver halide would be reduced, and the plate would be uniformly dark.

The plate still contains that portion of the original silver salt which has not been acted upon by the light or the developer. This must be removed before the plate is exposed to the light; otherwise, it, too, will be acted upon as previously described, and the image will be blurred or obliterated by more deposits of silver. This is done by a process known as *fixing*.

When it is seen by examination that the development has proceeded long enough, the plate is rinsed in water and placed in the *fixing bath*. This is a solution containing sodium thiosulphate ("sodium hyposulphite" or "hypo"), which is an excellent solvent for many silver compounds. The fixing bath soon dissolves from the gelatin film the silver bromide which remains unaffected by the light or the developer. The "chemistry" of the "fixing" process may be represented by the equation:

$$2AgBr + 3Na_2S_2O_3 \rightarrow 2NaAgS_2O_3, Na_2S_2O_3{}^* + 2NaBr.$$

This treatment is said to "clear" or "fix" the image. The plate is no longer sensitive to light. After thorough washing it is allowed to dry. The result is the *negative*.

The plate is now ready to be used in making *prints*. This is done by allowing sunlight to fall through the *negative* upon a sheet of sensitized paper, which may be regarded, for purposes of discussion, as paper covered with a film of albumen holding a deposit of silver chloride. The negative and the paper are placed film to film. The action of sunlight upon this paper is similar to that upon the plate. Exposure liberates silver.

$$2AgCl \rightarrow Ag_2Cl + \overline{Cl}$$
$$AgCl \rightarrow Ag + \overline{Cl}.$$

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* Formula of the crystals of the complex salt obtained from the solution.

As the dark portions of the negative which correspond to the light parts of the object transmit the fewer light rays (sunlight cannot penetrate the parts over which there is a deposit of silver), it is obvious that what is dark in the negative will be light in the *positive* and *vice versa*. The print will have the same shading as the object.

The print is then *toned* and *fixed*. Toning consists in imparting to the print a rich color by replacing part of the Ag_2Cl with gold from a solution of sodium chlor-aurate, $NaAuCl_4$.

$$3Ag_2Cl + NaAuCl_4 \rightarrow NaCl + 6AgCl + Au.$$

or

$$2Ag_2Cl + K_2PtCl_4 \rightarrow 2KCl + 4AgCl + Pt.$$

Fixing removes the unchanged silver salt, the operation being performed as previously described. After thorough washing the picture is dried and mounted.

"Retouching" is a process whereby blemishes are removed from both the negative and the positive by the use of India ink or colored pencils.

Experiment X.—Silver Nitrate and Organic Matter.

(*a*) Press a small crystal of silver nitrate between the thumb and forefinger for 10 or 15 seconds. After several hours, examine your finger (?).

(*b*) Using a solution of silver nitrate, write your name upon a sheet of paper with a pointed instrument. Expose the writing to the direct sunlight (?).

What is *lunar caustic?* What is the origin of this name?

Experiment XI.—Precipitation of Silver Chromate.

Add a solution of potassium dichromate to a silver nitrate solution. Describe the result. Equation?

Experiment XII.—Interaction Silver Salts and Potassium Cyanide.

(*a*) To a solution of silver nitrate add slowly, drop by drop, a potassium cyanide solution (poison) (?). Equation? Add the precipitant in excess (?). Pass hydrogen sulphide through this solution. Result? Is the silver ion present? Explain. Equation?.

What conclusion with regard to the formation of complex ions may be generally drawn when the precipitate dissolves in excess of the precipitant? Give examples.

(*b*) All silver salts are soluble in potassium cyanide. Test (?).

The bath ordinarily used for silver electroplating consists of a solution of potassium argenticyanide. Solutions of the simple salts do not give a coherent film.

$$\begin{aligned} AgNO_3 + 2KCN &\rightleftarrows KAg(CN)_2 + KNO_3 \\ KAg(CN)_2 &\rightleftarrows K^{\cdot} + Ag(CN)'_2 \\ Ag(CN)'_2 &\rightleftarrows Ag^{\cdot} + 2CN' \\ Ag' + \theta &\rightleftarrows Ag. \end{aligned}$$

Experiment XIII.—Analytical Reactions of Silver Salts.

(*a*) Compounds of silver heated on charcoal before the blow-pipe give a white metallic globule (?). Test (?).

(*b*) Dissolve a small crystal of chemically pure silver nitrate in distilled water. Test the reaction of the solution with litmus paper (?). Is the salt hydrolyzed by water? In this respect it approaches what group of metals?

What are your conclusions as to the relative chemical activity of silver and copper as metallic elements?

(*c*) Those reactions which are of particular importance in analytical chemistry are given in Exps. V and XII.

(*d*) Silver chloride is insoluble in either hot or cold water.

GOLD, AU.

At. Wt. 197.2 Sp. Gr. 19.3.

Experiment I.—Properties of Gold.

(*a*) Physical properties. Examine a piece of gold and state briefly the most obvious physical properties of the metal. (The student is reminded that the "commercial" metal is an alloy of gold and copper. The latter gives it greater hardness).

Record its melting point, specific heat and atomic heat. Calculate the atomic weight of gold by Dulong and Petit's Law. Pure gold is "24-carat." Explain the use of the word "carat." What is the composition of the American standard gold coin?

(*b*) Chemical properties. Is gold affected by free oxygen? Give reasons for your answer.

What is the valency of gold?

Direct a stream of hydrogen sulphide against a piece of pure gold (?). The negative result is indicative of its inacitivity. Gold is the least active of all of the familiar metals.

Does gold displace hydrogen from dilute acids? Before attempting to answer, see table of "Solution Tensions."

Gold combines with free chlorine, therefore, its solubility in *aqua regia* with the formation of auric chloride, $AuCl_3$.

Gold does not interact with any of the oxacids except selenic acid.

Experiment II.—Analytical Reactions of Salts of Gold.

(*a*) All compounds of gold are decomposed by heat with liberation of the metal. Test, using a solution of auric chloride (?).

(*b*) Hydrogen sulphide with solutions of $AuCl_3$ gives a black precipitate, auro-auric sulphide (Au_2S, Au_2S_3). This sulphide is insoluble in either hydrochloric or nitric acid, but soluble in *aqua regia*. It is also soluble in ammonium sulphide, forming an ammonium sulpho- or thioaurate.

(*c*) Ferrous sulphate gives a brown or purple precipitate of metallic gold. If the solution of the auric salt is dilute a bluish color is imparted to the mixture.

$$AuCl_3 + 3FeSO_4 \rightarrow Fe_2(SO_4)_3 + FeCl_3 + Au.$$

(*d*) Stannous chloride gives with solutions of auric chloride a precipitate or coloration which varies in color from reddish-brown to purple. The color is due to the presence of a compound of uncertain composition, known as the *purple of Cassius.*

The test may be made as follows: Add a ferric chloride solution to a solution of stannous chloride until the latter has a permanent yellow color. Add a drop of this solution to an auric chloride solution (?), or dip a glass rod into the former solution, and then into the latter (?).

(*e*) Other reducing agents, like oxalic acid and potassium nitrite, when warmed with solutions of $AuCl_3$, precipitate the gold. If the former reagent is used, the gold is deposited in a spongy form similar to that used by dentists.

$$2AuCl_3 + 3H_2C_2O_4 \rightarrow 6HCl + 6CO_2 + 2Au.$$
$$2AuCl_3 + 3KNO_2 + 3H_2O \rightarrow 3KNO_3 + 6HCl + 2Au.$$

PROBLEMS.

1. How much cupric oxide is formed by heating 10 grams of copper in the air?

2. How much cuprous oxide can be prepared, theoretically, by boiling 10 grams of cupric sulphate with a solution of potassium hydroxide and glucose?

$$2CuSO_4.5H_2O + 4KOH \rightarrow Cu_2O + O + 2K_2SO_4 + 12H_2O.$$

3. Calculate the percentage of copper in *malachite*, $Cu(OH)_2,Cu(CO_3)$ In *azurite*, $Cu(OH)_2,2CuCO_3$.

4. If 2 grams of silver chloride yield 1.505 grams of silver, what is the atomic weight of silver?

5. Calculate the quantities of silver and gold which can be deposited from their respective solutions by the gram-atomic weight of copper. By 1 gram equivalent. By 1 gram of copper.

6. The same electric current passes through separate solutions of silver nitrate and copper sulphate. The electrodes in each case are plates of platinum. The cathode in the copper sulphate solution increased 0.636 gram in weight. How much did the cathode in the silver nitrate solution increase in weight?

7. One coulomb of electricity deposits 0.0011175 gram of silver. This quantity is known as the *electro-chemical* equivalent of silver. How many coulombs are required for the deposition of one gram equivalent of silver? Of any substance? Calculate the electro-chemical equivalent of copper.

CHAPTER XXVI.

ALKALINE EARTH METALS.

(Glucinum, Gl.	9.1)
Magnesium, Mg.	24.36
Calcium, Ca.	40.1
Strontium, Sr.	87.6
Barium, Ba.	137.4
(Radium, Rd.	225.)

The metals of this family are called the "alkaline-earth" metals because they form the transition from the "alkalies" to the "earth" metals, such as aluminum, gallium, etc.

None of the elements of the family occur in nature in the uncombined condition, and have only in more recent years been prepared from their compounds. With the exception of **magnesium,** they are seldom isolated. In the case of glucinum this is due largely to the comparative rarity of its compounds. **Calcium, strantium** and **barium** whose compounds are abundant, are seldom prepared in the pure state save in very small quantities because of the extreme difficulty in isolating them, and owing also to the fact that they are of little commercial importance.

Although these elements are brought into the same family by the periodic grouping and possess many marked similarities, yet they do not form an altogether homogeneous and coherent group.

Glucinum and magnesium are white metals which do not rust (oxidize) rapidly in the air, while calcium, strontium and barium, under similar conditions, quickly lose their silver-white luster. Glucinum does not decompose water; magnesium displaces hydrogen from boiling water; and the other metals decompose water spontaneously at ordinary temperatures, forming hydroxides.

Glucinum and magnesium resemble zinc and cadmium and differ from calcium, strontium and barium in that their sulphates are readily soluble in water, but these relations are reversed in the case of their sulphides which are hydrolyzed by water. Glucinum differs from magnesium and resembles zinc in that its hydroxide is acidic as well as basic, i.e., is soluble in sodium or potassium hydroxide.

Calcium, strontium and barium bear a much closer resemblance to each other in most of their physical and chemical properties than to either glucinum or magnesium. Their hydroxides show an increasing solubility* and alkalinity in the order named. These solutions, which are very dilute, owe their strong alkalinity to the high degree of ionization (see

* 200, 630, and 2,200 parts of the hydroxides, respectively, dissolve in 1,000,000 parts of water.—Smith.

table) which they undergo. The order of the solubility of the sulphates of these three metals is reversed—2100, 110 and 2.3 parts, respectively, being soluble in 1,000,000 parts of water.

All of these metals form an oxide of the type MO; calcium, strontium and barium also form peroxides of the type MO_2. The oxides combine with water, forming hydroxides.

When the nitrates of calcium, strontium, and barium are heated they are decomposed, yielding the oxides of the metals, nitrogen peroxide and oxygen.

The carbonates which are insoluble, when heated, are decomposed into the oxide of the metal and carbon dioxide.

The metals of the family usually exhibit a valence of two.

Radium, one of the recently discovered elements, has never been isolated. It is a "radio-active" substance which appears to belong to this family. It exhibits a valence of two in those of its salts which have been investigated.

GLUCINUM, Gl.

At. Wt. 9.1 Sp. Gr. 1.8.
See lecture-notes or text-book.

MAGNESIUM, Mg.

At. Wt. 24.36 Sp. Gr. 1.74.

Experiment I.—Properties of Magnesium.

(*a*) Examine the elementary substance in the forms of "ribbon," wire and powder. Scrape a piece of magnesium ribbon, and note its color and luster.

(*b*) Combustion of magnesium in the air. Introduce a piece of the ribbon into the flame with the forceps (?). What is the product? Equation?

Apply the flame (caution) to a small pinch of magnesium powder upon an iron plate (?). Account for the difference in the speeds of the reactions.

Note.—Powdered magnesium is frequently used as one of the components of "flash-light powder" for use in photography.

(*c*) Solubility in acids. Treat individually small pieces of magnesium ribbon with dilute sulphuric acid (?), hydrochloric acid (?), nitric acid (?) and acetic acid (?). Express each reaction by an equation.

Experiment II.—Magnesium Salts.

Examine the different salts of magnesium (end shelf), noting the obvious physical properties. Give the name, formula, color and solubility* of each salt. Tabulate the foregoing data.

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*See Comey's Dictionary of Chemical Solubilities, and Seidell's Solubilities of Inorganic and Organic Substances.

Experiment III.—Hydrolysis of Magnesium Chloride.

Ascertain by experiment whether magnesium chloride dissolves completely in water (?). Test the solution with litmus paper (?). Explain. Equation?

Place several small crystals of the salt in a dry test tube, and heat strongly. Test the reaction of the evolved vapors, and the liquid which condenses in the tube toward litmus paper (?). Explain. Equation?

Give the formula for *carnallite.*

Experiment IV.—Precipitation of Magnesium Hydroxide and its Solubility in Ammonium Compounds.

(*a*) To 10 cm.^{3} of solution of magnesium sulphate add a solution of sodium hydroxide or potassium hydroxide (?). Equation?

(*b*) Repeat (*a*) using ammonium hydroxide as the precipitant. Observe the character of the precipitate. Express the reaction by an equation. Is the precipitation of the magnesium complete? Before attempting to answer this last question, add a strong solution of ammonium chloride (note that this is one of the "products" in the above reaction) in large excess. Explain the disappearance of the precipitate in terms of the ion- or solubility-product constant.

(*c*) Can magnesium hydroxide be precipitated in the presence of an excess of an ammonium salt?

Experiment V.—Precipitation of Hydrated Basic Carbonate of Magnesium; Its Solubility in Ammonium Compounds.

(*a*) Add a slight excess of a sodium carbonate solution to 10 cm.^{3} of a solution of magnesium sulphate. The composition of the precipitate varies with conditions.

(*b*) Repeat (*a*), using ammonium carbonate instead of sodium carbonate. Add an excess of a strong solution of ammonium chloride. Result? Equation?

(*c*) Can the basic carbonate of magnesium be precipitated in the presence of an excess of an ammonium salt?

Experiment VI.—Preparation of Magnesium Chloride.

To 15 cm.^{3} of a dilute solution of hydrochloric acid add an excess of basic magnesium carbonate, filter, evaporate to small volume and crystallize. Equation? What is the formula of the crystallized salt?

Experiment VII.—Analytical Reactions of Magnesium Salts. Precipitation of Ammonium Magnesium Phosphate.

To 10 cm.^{3} of a solution of a soluble magnesium salt add an excess of ammonium chloride, then add cautiously 2 cm.^{3} or 3 cm.^{3} of ammonium hydroxide or an equal volume of a solution of ammonium carbonate. (Why do neither of the latter substances produce a precipitate?) To the clear solution thus obtained add a disodium hydrogen phosphate

(Na_2HPO_4) solution until precipitation ceases. Describe the precipitate. Express the reaction by an equation.

When ammonium magnesium phosphate is ignited it is converted into the anhydrous pyrophosphate of magnesium.

$$(2NH_4MgPO_4, 6H_2O \rightarrow Mg_2P_2O_7 + 2NH_3 + 13H_2O).$$

What is the color and valence of the magnesium ion?

CALCIUM, Ca.

At. Wt. 40.1 Sp. Gr. 1.85.

Experiment I.—Properties of Calcium.

(*a*) Enumerate the most obvious physical properties of the metal.
(*b*) Does it interact with water? Equation?
(*c*) Will it burn in the air? Equation?

Note.—The product of the combustion is a mixture of the oxide and the nitrite (Ca_3N_2). Compare with the combustion of magnesium in air.

Experiment II.—Action of Acids upon Calcium Carbonate.

(*a*) Recall or repeat Exp. II (*c*), "Carbon." Indicate by an equation the action of hydrochloric acid upon marble (impure calcium carbonate).

(*b*) Test a small quantity of powdered marble with dilute sulphuric acid, and note the effect. Equation?

(*c*) Repeat (*b*) substituting nitric acid for sulphuric acid.

Experiment III.—Preparation of Calcium Oxide (Quicklime).

Ignite about 3 grams of powdered marble for 15 to 20 minutes in an *open* crucible placed upon a pipe-stem triangle. Maintain the crucible and contents at the highest temperature obtainable with the aid of a blast-lamp. Occasionally stir the mass with a platinum wire. When the mass has cooled, add about 10 cm.^{3} of water; stir the mixture (?). Test reaction of the liquid with litmus paper (?). Does water act upon marble? Add a few drops of hydrochloric acid to the above mixture (?). How do the results compare with the action of acid upon marble? What are your conclusions as to the identity of the substance in the crucible? The decomposition of the marble by heat is a *reversible* reaction. How may it be brought to a condition of equilibrium? How may it be reversed? How may it be reversed without altering the temperature? What precautions must be taken in the construction of a lime-kiln that the complete decomposition of marble into calcium oxide and carbon dioxide may be insured? Indicate by equations the chemical equilibria involved in the above decomposition.

Experiment IV.—Preparation and Properties of Calcium Hydroxide. Lime-Water.

(*a*) Pour 5 cm.^{3} of distilled water upon 8 grams of quicklime in a porcelain dish, and note the results (?). The foregoing process is known as the "slaking" or "slacking" of lime. The product is known as calcium hydroxide. Express the reaction by an equation. What is "mortar"? What is "air-slacked" lime?

(*b*) Solubility* and effect of calcium hydroxide upon litmus. Put 4 or 5 grams of the calcium hydroxide prepared in (*a*) into a flask or bottle containing 200 cm.^{3} of distilled water, cork tightly, shake vigorously from time to time, and allow the mixture to stand until the solution has become clear, when the latter may be decanted, drawn off with a siphon or removed with a pipette. If too much time is consumed in allowing the mixture to settle, it may be filtered rapidly, and the clear liquid (lime-water) used for the following experiments.

(*c*) Test the action of the solution upon litmus paper (?). The result indicates the presence of what ion? Explain.

(*d*) Recall or repeat Exp. II (*d*), "Carbon." Equations?

To a piece of *old mortar* in a test tube add dilute hydrochloric acid. Identify the gas (?). What chemical action is involved in the "hardening" of mortar?

(*e*) Recall or repeat Exp. V "Carbon." Equations? When is water said to possess "temporary hardness"? It is due to the presence of what salt?

Experiment V.—Calcium Salts.

Repeat Exp. II "Magnesium," substituting the word calcium where the word magnesium appears.

Experiment VI.—Preparation of Calcium Salts.

(*a*) Calcium chloride. Suggest by an equation such a method for the preparation of calcium chloride from one of its salts as will not involve the simultaneous formation of any other salt, acid or base. Is calcium chloride deliquescent or efflorescent? It is frequently used for what purpose in connection with the manipulation of gases?

(*b*) Calcium hypochlorite. Describe a method for the preparation of this salt. (Suggestion, see Exp. III (*a*), "Chlorine.") Equation? What is "bleaching powder"?† Its formula?

Experiment VII.—Dehydration of Gypsum. Plaster of Paris.

(*a*) Heat a few grams of powdered *gypsum* or a small piece of a *selenite* crystal ($CaSO_4 . 2H_2O$) in a test tube and record the obvious results. Pulverize the residue and ascertain whether it will become solid when

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* At 18°, 600 parts of water by weight dissolve 1 part of the hydroxide; at 100°, about twice as much water is required to dissolve the same quantity of salt.—Seidell.

† The probable formula of bleaching powder is $CaCl\ (ClO)$—a mixed salt rather than an equi-molar mixture of $CaCl_2$ and $Ca(OCl)_2$. This view is supported by the fact that $CaCl_2$ cannot be dissolved out with alcohol, nor is the salt deliquescent as is calcium chloride ($CaCl_2$). The ions Ca'', Cl', and ClO' are present in a solution of the salt.

mixed with a little water to form a paste and allowed to stand (?). See whether gypsum itself will act in the same way with water (?). Equations?

Note.—If all of the water is removed from gypsum by heating or the temperature is allowed to rise much above 125°, the product when mixed with water does not "set" quickly.

(*b*) Make a thick paste by mixing a little water with "plaster of Paris." Place the paste upon a glass plate and make a cast of a coin. Chemically, what is "plaster of Paris?" Probable formula?

Experiment VIII.—Solubility of Phosphates of Calcium.

(*a*) Ascertain whether or not the tertiary orthophosphate of calcium ($Ca_3(PO_4)_2$) is soluble in water? Would such a salt make a good fertilizer? Reasons for your answer?

(*b*) Repeat (*a*) using primary calcium phosphate ($Ca(H_2PO_4)_2$. What is "superphosphate of lime"? Its use?

Experiment IX.—Analytical Reactions of Calcium Salts.

(*a*) Flame test. Introduce a small quantity of calcium chloride into the Bunsen flame by means of a platinum wire (?). Examine the flame with a spectroscope, noting particularly the presence of two bands—a red and a green one—which impart the brick-red color to the flame.

(*b*) (Use a dilute solution of pure calcium chloride for the following tests.) Examine such solutions of calcium salts as are found on the end shelf. What is the color of the calcion? Its valence? Justify your conclusions.

(*c*) Calcium carbonate. To a portion of the solution containing the calcion add a slight excess of an ammonium carbonate solution (?). Warm the solution if necessary to procure complete precipitation. Express the reaction by an equation. Filter, spread the filter paper with precipitate upon a glass plate and divide the precipitate into two parts. Treat one part with hydrochloric acid (?) and the other with dilute acetic acid (?). Equations? What are your conclusions as to the relative strength of acetic and carbonic acids? Confirm your inference by giving the degrees of ionization in .1 normal solutions of the acids. Explain in terms of the "electrolytic dissociation theory" how the insoluble salt of a "weak" acid is dissolved by a stronger acid.

(*d*) Calcium oxalate. Add an excess of an ammonium oxalate solution to a dilute solution of calcium chloride (?). Equation? Filter and divide precipitate into two parts. Test the precipitate as in (*c*). Interpret results.

Explain the difference in behavoir of the oxalate and carbonate of calcium toward acetic acid, taking into account the difference in solubility of the two salts, and the behavior of oxalic acid and carbonic acid, respectively. Why was ammonium oxalate used as the preciptant in preference to oxalic acid (recall or repeat Exp. II (*c*), "Chemical Equilibrium")? Under what conditions may calcium oxalate be precipitated from a calcium chloride solution? Explain.

(*e*) I. Calcium sulphate. (e,I. Repeat Exp. II (*b*), "Chemical Equilibrium.")

(*e*) II. To a dilute solution of calcium chloride add a slight excess of dilute sulphuric acid (?) Equation? Filter and divide the filtrate into two parts. Add sufficient ammonium hydroxide to one portion to barely neutralize the free acids (determine the "end point" by means of litmus paper). Now add ammonium oxalate to the neutralized solution (?). Explain the precipitation of calcium oxalate. Which is the more soluble—the sulphate or oxalate of calcium? Give the actual solubilities of each. (See works to which you have been referred previously.)

(*e*) III. "Permanent hardness" of water. Boil the second portion of the filtrate from (*e*), II. Compare the negative result with that obtained in Exp. IV (*e*). To the above solution add a solution of sodium carbonate (?). Equation? Devise a method for proving that the precipitate is calcium carbonate (?). Is the sulphate or the carbonate more soluble (?). Reasons for your answer? Give the actual solubilities of the two substances. Can "permanent hardness" be removed by boiling? Give one method for removing it. What are some of the objections to "hard water" for domestic and technical use?

STRONTIUM, Sr.

At. Wt. 87.6 Sp. Gr. 2.54.

Experiment I.—Properties of Strontium and its Salts.

Strontium is a yellowish-white, rather tough metal which slowly oxidizes spontaneously in the air. It burns when heated in the air, and decomposes water at ordinary temperatures. It is malleable and ductile and fuses at red heat.

The physical and chemical properties of the compounds of strontium are very similar to those of calcium.

Experiment II.—Strontium Salts.

Repeat Exp. II, "Magnesium," substituting the word strontium for magnesium.

Experiment III.—Analytical Reactions of Strontium Salts.

(*a*) Flame test. Dip a platinum loop into a solution of strontium chloride and hold it in the Bunsen flame (?). Examine the flame with a spectroscope and make a sketch of the spectrum showing the position of the lines with reference to the sodium lines.

Note.—Anhydrous strontium is mixed with charcoal, sulphur and potassium chlorate to make "red fire."

(*b*) Strontium carbonate. Add ammonium hydroxide and ammonium carbonate to a dilute solution of strontium chloride (?). Equation? Filter, wash the precipitate and test the action of acetic and hydrochloric acids upon it (?). Equations?

(*c*) Strontium sulphate. To a solution containing strontium add a small amount of a solution of calcium sulphate; heat to boiling, and if no precipitate appears immediately, let the mixture stand for 10 or 15 minutes. Explain why the precipitate forms so slowly. What do you infer regarding the relative solubilities of calcium and strontium sulphates. Give the actual solubilities of each.

What is the color of the strontium ion? Its valence?

BARIUM, Ba.

At. Wt. 137.4 Sp. Gr. 3.6.

Experiment I.—Properties of Barium and its Salts.

Barium is a bright yellow metal which readily oxidizes spontaneously in the air. It decomposes water energetically at ordinary temperatures. The metal is malleable and ductile and fuses at red heat.

The physical and chemical properties of the compounds of barium resemble those of calcium and strontium.

Experiment II.—Barium Salts.

Same as Exp. II, "Strontium."

Experiment III.—Water of Hydration in Barium Chloride.

A crucible with the lid, which has been cleaned, is placed on a pipestem triangle and heated with the Bunsen burner for a few minutes. Cool, and determine carefully the weight of the crucible. Weigh into crucible accurately about 3 grams of pure crystallized barium chloride. Place the crucible with its contents in an air bath at 120° to 130° C. for about one hour, then cool for 10 minutes and weigh; or the crucible and its contents may be placed on a triangle and heated gently with a small Bunsen burner flame. The temperature is gradually raised until the crucible attains a low red heat at which it is maintained for 10 minutes when it is cooled and weighed as per above directions. The heating and weighing is repeated until the weight is constant.

Record your results as follows: Grams.

Weight of Xble + barium chloride =
Weight of Xble alone =
  Weight of barium chloride taken =
Weight of Xble + contents before heating =
Weight of Xble + contents after heating =
  Weight of water found =
Per cent. of water in barium chloride =
Theoretical per cent. =
  Error =

Experiment IV.—Analytical Reactions of Barium Salts.

(*a*) Flame test. Same as Exp. III (*a*), "Strontium."

Note:—Barium chlorate is used with charcoal and sulphur to prepare "green fire."

(*b*) Barium carbonate. Same as Exp. III, *b*, "Strontium."

(*c*) Barium chromate. To a dilute solution of barium chloride add a solution of potassium chromate (?). Ascertain whether the precipitate is soluble in dilute acetic acid. In hydrochloric acid.

Note.—Neither calcium nor strontium chromate is precipitated from dilute solutions acidified with acetic acid.

(*d*) Barium sulphate. Add dilute sulphuric acid to a barium chloride solution (?). Equation?

To 10 cm.^{3} of a solution of barium chloride add 20 cm.^{3} of a clear saturated solution of strontium sulphate (prepared by shaking the salt with distilled water and filtering) (?). Which is the more soluble—strontium or barium sulphate?

Arrange the sulphates of calcium, strontium and barium in the order of decreasing solubility. Give the actual solubility of each.

Experiment V.—Detection of the Alkaline Earth Metals in a Mixture.

(*a*) Give two methods for *distinguishing* the compounds of the metals of this group.

(*b*) How may the carbonate of magnesium be *separated* from the carbonates of the other three metals of this group?

Are the carbonates of calcium, strontium and barium soluble in acetic acid?

State how barium may be separated from calcium and strontium. How may the presence of calcium and strontium in a solution of their compounds be proven?

(*c*) If a solution of the compounds of the four metals of this group were given you, how would you proceed to prove their presence? Make a statement of your proposed method and submit it to the instructor for inspection.

(*d*) Procure an "unknown" solution containing two or more of the elements of this group and make an analysis of same according to the method proposed in (*c*).

RADIUM, Rd.

At. Wt. 225 Sp. Gr. (?)
(See lecture notes and references.)

EXERCISES.

1. Chemically, what is (a) asbestos? (b) meerschaum? (c) olivine? (*d*) serpentine?

2. What is (a) chalk? (b) calcite? (c) limestone? (d) cement (Portland)? (e) apatite?

3. What is (a) celestite? (b) strontianite?

4. What is (a) witherite? (b) heavy spar or barite?

PROBLEMS.

1. Calculate the percentage of barium in barium chloride.

2. Calculate the weight of sulphuric acid necessary to precipitate the barium as barium sulphate from a solution containing .5 gram of barium chloride, $BaCl_2.2H_2O$?

3. Calculate the percentage of chlorine in barium chloride.

4. Calculate the weight of silver nitrate required to precipitate the chlorine as silver chloride from a solution containing .7 gram of barium chloride.

CHAPTER XXVII.

Zinc,	Zn,	65.4
Cadmium,	Cd,	112.4
Mercury,	Hg,	200.0

Zinc, cadmium and **mercury** form the secondary family of the alkaline earths. The elementary substances of this family and their corresponding compounds possess many similar properties. Their relation to magnesium, calcium, strontium and barium resembles the relationship existing between the alkalies and copper, silver, and gold.

These three elementary substances are lustrous metals of high specific gravity and are found in combination as *minerals*, which occur usually as *ores* in the older crystalline rocks. *Smithsonite*, $ZnCO_3$, *sphalerite* or *zinc blende*, ZnS, and *calamine*, $H_2Zn_2SiO_5$, are the principal minerals which contain **zinc. Cadmium** is found in small quantities in those ores in which zinc is the chief metal present. It is also found in the rare mineral, *greenockite*, CdS. Small quantities of **mercury** are found in minute globules disseminated through the pores of those rocks where the most important mineral containing mercury, namely, the red sulphide, *cinnabar* (HgS), occurs. Alloys of silver and gold, known as *amalgams*, are also found *native*. The metallurgy of these substances is comparatively simple—all three of the metals being obtained easily by roasting the ores alone or in mixture with carbon, in ovens, and condensing the vapors as the metals volatilize at high temperatures.

In their physical characteristics, the elements of this family are certainly metallic in their nature. Zinc, which has the smallest atomic weight of the three, is less positive than the other two. The appended table shows the interesting gradation of properties, physical and chemical, with increasing atomic weight; for example, the boiling points and the melting points decrease with increase of atomic weight. It will be remembered that the non-metallic elements behave in a contrary manner and that the conduct of the alkali metals is very similar.

Zinc is a bluish-white crystalline metal, brittle at ordinary temperatures, but malleable at 120°–150°. Cadmium is a white, lustrous metal, fairly soft, ductile and malleable. Mercury is a heavy, silvery, lustrous liquid.

At ordinary temperatures zinc is acted upon but superficially by moist air, but cadmium is scarcely affected and mercury not at all. However, all three of the metals are converted into oxides when heated in the air.

Finely divided zinc will set free hydrogen from water at ordinary temperature, but massive zinc and cadmium act upon water only at red heat. Mercury has no effect upon water.

The metals of this family can be deposited from solutions of their salts by the electric current or by metals above them in the electrochemical series, and they will displace other metals below them in the series.

These metals are bivalent—mercury being the only one which forms two series of salts (mercur*ous* and mercur*ic* compounds), which differ from each other in the proportions in which mercury is contained in them. The same tendency is shown to a slight extent by cadmium.

Zinc dissolves easily in dilute acids, and is attacked by the caustic alkalies when the latter are warmed. Hydrogen is evolved in both cases. Cadmium dissolves less readily in acids, but is not soluble in solutions of the caustic alkalies. Mercury does not dissolve in hydrochloric acid or dilute sulphuric acid; concentrated sulphuric acid, when hot, however, attacks it and liberates sulphur dioxide; concentrated nitric acid acts upon the metal forming mercuric nitrate; dilute nitric acid yields mercurous nitrate. The caustic alkalies do not attack mercury.

The *oxides* and *hydroxides* of zinc, cadmium and mercury are soluble in acids, yielding salts, in solutions of which the metals are positive ions. A few zinc salts, known as *zincates* and of the type Na_2ZnO_2, in which zinc is in the negative ion, are formed by the interaction of zinc, its oxide or hydroxide, with strong basic hydroxides.

$$2NaOH + Zn \rightarrow Na_2ZnO_2 + \overline{H_2}$$
$$2NaOH + Zn(OH)_2 \rightarrow Na_2ZnO_2 + 2H_2O.$$

In this respect zinc resembles aluminum, lead and a number of other metals which can display both metallic and non-metallic properties.

The *chlorides*, *nitrates* and *sulphates* are soluble in water, but the *oxides*, *carbonates* and *phosphates* are insoluble in water. The *chlorides* are comparatively volatile and the *hydroxides* lose water forming the oxides.

The compounds of zinc, cadmium and mercury do not give color to the borax bead.

The following table emphasizes the similarity in the properties of the three metals and their corresponding derivatives.

	Zinc.	Cadmium.	Mercury.
Atomic Weight,	65.4	112.4	200.0
Specific Gravity,	7.1	8.6	13.59, (0°)
Atomic Volume,	9.1	12.9	14.7
Melting-point,	419°	321.7°	—38.85°
Boiling-point,	920° (?)	778°	357°
*Vapor Density,	65.5	112	200.3

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* These vapor density determinations indicate that the molecular weight and the atomic weight of each of the three elementary substances, when they are in the state of vapor, are identical. If our conclusions, as to the relative weights of these atoms, are correct, it is obvious that zinc, cadmium and mercury, on changing from the liquid to the gaseous state, separate into individual atoms. Sodium and potassium behave in a similar manner.

Oxides,	ZnO,H_2O	CdO,H_2O	HgO
H. of F.	82,600 cal.	65,700 cal.	22,000 cal
Chlorides,	$ZnCl_2$	$CdCl_2$	$HgCl_2$
H. of F.	97,200 cal.	93,200 cal.	54,500 cal.
Sulphides,	ZnS	CdS	HgS
H. of F.	(Zn,S, Aq), 39,600 cal.	(Cd, S, Aq.), 32,400 cal.	Hg,S, 16,200 cal. (?)
Sulphates,	$ZnSO_4$	$CdSO_4$	$HgSO_4$.
H. of F.	230,000 cal.	221,000 cal.	. . . . . .

Note.—It is maintained by many that if we were able to make vapor density determinations at very high temperatures, we should discover that all diatomic molecules are converted into monatomic ones.

ZINC, Zn.

At. Wt. 65.4 Sp. Gr. 7.1.

Experiment I.—Properties of Zinc.

(*a*) Clean part of a piece of zinc with sand-paper or a file. Color?

(*b*) Is zinc hard or soft (use the point of a knife blade)?

(*c*) Does zinc tarnish when exposed to the moist air?

(*d*) Is zinc soluble in sulphuric acid? In hydrochloric acid? Equations?

(*e*) Place about 1 $cm.^3$ of zinc dust in a test tube, and add 5 $cm.^3$ of a strong solution of sodium hydroxide. Heat the mixture carefully and test the evolved gas with a flame. Results? Identify the gas. The solution contains *sodium zincate*, Na_2ZnO_2. Express the action by an equation.

(*f*) Recall or repeat Exp. XI (*a*), "Electrolysis and Electrical Equivalents."

(*g*) Enumerate some of the uses of zinc. What is "galvanized" iron?

Experiment II.—(Quant.) Determination of the Atomic Weight of Zinc.

(*a*) Proceed as in Exp. XIII, "Hydrogen." Calculate the weight of hydrogen collected. Determine the atomic weight of zinc referred to $H = 1$, remembering that zinc is bivalent. Write the reaction.

(*b*) The specific heat of zinc is 0.093. Calculate the atomic weight of zinc by Dulong and Petit's Law. State the latter.

Experiment III.—Preparation of Hydrated Zinc Chloride.

Dissolve two or three small pieces of "granulated" zinc in hydrochloric acid, dilute with an equal volume of water, filter and evaporate the filtrate to oily consistency in a porcelain dish. Cool, and examine the product (?). Equation?

Experiment IV.—Preparation of Hydrated and Dehydrated Zinc Sulphate.

(*a*) Suggest a method for the preparation of hydrated zinc sulphate, $ZnSO_4.7H_2O$. Equation?

(*b*) How may the above salt be dehydrated? At what temperature does it lose all or a part of its water of hydration. (Consult your text-book)? What is *white vitriol?*

Experiment V.—Precipitation and Behavior of Zinc Hydroxide. Formation of a Zincate.

(*a*) To a dilute solution of zinc sulphate add a sodium hydroxide solution drop by drop and shake. Result? What, probably, is the precipitate? Equation? Filter, and suspend the precipitate in water in a test tube by punching a hole through the apex of the filter paper, and directing a stream of water from the water-bottle upon the precipitate. Divide the mixture into two parts.

(*b*) To one part add hydrochloric acid? Equation? Does the zinc hydroxide behave in this reaction as a base or an acid?

(*c*) To the second part of the mixture from (*a*) add an excess of the sodium hydroxide solution (?). The compound formed by the interaction of zinc hydroxide and sodium hydroxide is *sodium zincate*, Na_2ZnO_2. Ionic equation? Does this reaction indicate that zinc hydroxide possesses acidic or basic properties? Is the zinc a part of the anion or cation?

What are your inferences as to the "strength" of zinc hydroxide as a base?

Experiment VI.—Preparation and Properties of Zinc Hydroxycarbonate and Zinc Oxide.

(*a*) Add slowly a solution of sodium carbonate to a dilute solution of zinc sulphate (?). Note the evolution of gas as the precipitate forms. Prove that the escaping gas is carbon dioxide (?). Boil the mixture, taking care that the precipitant is in excess; filter, and wash the precipitate. Test a small portion of the precipitate with hydrochloric acid. Is carbon dioxide evolved? Account for the evolution of this gas during the formation of the precipitate. Express by ionic equations the precipitation of the basic zinc carbonate.

(*b*) Heat the other portion of the precipitate from (*a*) to redness in a porcelain crucible until a portion removed and tested with hydrochloric acid does not effervesce. Note the color of the residue when hot and when cold (?). Equation? Reserve the zinc oxide for Exp. VIII (*a*).

Experiment VII.—An Experimental Study of Ionic Equilibrium and "Concentration Effect."

(*a*) Place 5 cm.^{3} of zinc acetate, zinc sulphate and zinc chloride in separate test tubes. Test each solution with litmus paper (?). Saturate the solutions with hydrogen sulphide. Results? Equations? Are these reactions reversible theoretically; i.e., does the acid which is formed simultaneously with the zinc sulphide in each case dissolve the latter to a larger or smaller degree? Will the amount of zinc sulphide dissolved vary with the *activity* of the different acids? The answers to these latter questions may be ascertained by two different experimental methods. Proceed as follows:

Filter separately the contents of the tubes and preserve each filtrate in a separate tube which should be marked to prevent confusion.

Compare the rates at which zinc sulphide (the precipitate) dissolves in dilute acetic acid, dilute sulphuric acid and dilute hydrochloric acid. Results? What are your inferences as to the relative "*activities*" of the three acids?

Confirm your inferences by adding ammonium hydroxide to each filtrate in the marked tubes. The zinc in solution is now precipitated as zinc sulphide (the ammonium hydroxide merely neutralizes the free acid). In which solution (filtrate) do you find the largest amount of zinc? The least amount? Do these results confirm your previous conclusions as to the relative strength (activity) of the three acids?

(*b*) To 5 cm.^{3} of a dilute solution of zinc sulphate add a few drops of sulphuric acid. Pass hydrogen sulphide into the solution. If a precipitate forms, add more acid, *drop* by *drop*, until hydrogen sulphide does not produce a precipitate. The addition of sulphuric acid increases the concentration of what ions? Does this influence the degree of ionization of the hydrogen sulphide? When there is an excess of free acid present in the solution is the hydrogen sulphide chiefly in the *molecular condition* or is it largely *dissociated?* Is chemical action an interaction of ions or molecules ordinarily? Show by ionic equation the failure of hydrogen sulphide to precipitate zinc sulphide in the presence of a free inorganic acid. Now add an excess of a sodium acetate solution (zinc acetate is soluble), and pass hydrogen sulphide into the solution if a precipitate of zinc sulphide does not form at once. Account for the formation of the precipitate. Express the various interactions by ionic equations.

Experiment VIII.—Analytical Reactions of Zinc Salts.

(*a*) Heat a small piece of zinc on charcoal in the oxidizing flame (?). Moisten the incrustation which is formed on the charcoal with a drop of cobalt nitrate, and heat again or place a small pinch of the zinc oxide prepared in Exp. VI (*b*) on the charcoal and proceed as above. Result? Equations? (The formula of the green compound, *Rinman's green*, is $CoZnO_2$.)

Does the zinc manifest acidic or basic properties in this reaction? Reasons for your answer?

(*b*) Test a dilute solution of zinc sulphate with litmus paper (?). Account for the result.

(*c*) Ammonium hydroxide produces in neutral solutions of zinc salts a partial precipitation of zinc hydroxide which is soluble in excess of the precipitant and ammonium chloride, forming $Zn(NH_3)_4.Cl_2$ or $Zn(NH_3)._4(OH)_2$. If this solution is treated with ammonium sulphide, $(NH_4)_2S$, zinc sulphide is formed. Equations?

(*d*) Add a slight excess of ammonium sulphide to several cm.^{3} of a solution of zinc sulphate. Result? Equation? Filter, and wash the precipitate with water. Divide the precipitate into two parts. Try its solubility in dilute hydrochloric acid, and acetic acid (?). Equations?

Why was ammonium sulphide used instead of hydrogen sulphide in the above reaction?

What is the color of the zinc ion? Its valence?

CADMIUM, Cd.

At. Wt. 112.4 Sp. Gr. 8.6.

Experiment I.—Properties of Cadmium.

(*a*) Examine a piece of the metal and tabulate its obvious physical and chemical properties.

(*b*) Will cadmium displace zinc from a solution of a salt of the latter (Note their relative positions in the electro-chemical series)?

(*c*) Calculate the atomic weight of cadmium by Dulong and Petit's Law, the specific heat of cadmium being 0.054.

(*d*) Give the composition of "Wood's Metal." (See Appendix). Repeat or review Exp. II. "Bismuth."

(*e*) Enumerate some of the chief uses of the metal.

Experiment II.—Properties of Cadmium Salts.

Same as Exp. II "Magnesium."

Experiment III.—Precipitation and Solubility of Cadmium Hydroxide.

Repeat Exp. V (*a*) and (*b*), substituting the word cadmium where the word zinc appears. Equations? Compare the behavior of the zinc and the cadimum compounds (?).

Experiment IV.—Precipitation of Cadmium Carbonate. Preparation of Cadmium Oxide.

(*a*) To 10 cm.^{3} of a dilute solution of cadmium chloride add a small excess of sodium carbonate. Result? Equation? Filter, and wash the precipitate. Test a small portion of the precipitate with hydrochloric acid (?). Equation?

(*b*) Heat the rest of the precipitate from (*a*) to redness in a crucible until a portion removed and tested with hydrochloric acid does not effervesce. Note the color of the residue when hot and when cold (?). Equations? Reserve the cadmium oxide for Exp. V (*a*).

Experiment V.—Analytical Reactions of Cadmium Salts.

(*a*) Mix a portion of the cadmium oxide obtained from Exp. IV (*b*), or some other cadmium compound, with anhydrous sodium carbonate, and heat the mixture on a piece of charcoal in the reducing flame. During the preliminary stages of the reduction, note the characteristic incrustation (?). Continue the process until small metallic globules (?) make their appearance.

(*b*) Same as Exp. VIII (*b*) "Zinc."

(*c*) Ammonium hydroxide precipitates cadmium hydroxide from solutions of cadmium salts. The hydroxide is soluble in excess, forming salts such as $Cd(NH_3)_4.SO_4$ or $Cd(NH_3)_4.(OH)_2$. If this ammoniacal solution is treated with a solution of potassium cyanide, KCN, a soluble complex salt, $K_2.Cd(CN)_4$ is formed.

(*d*) Saturate a solution of cadmium chloride with hydrogen sulphide (?). Equation? Is the reaction reversible? Answer this question by testing the solubility of cadmium sulphide in dilute hydrochloric acid. Will hydrogen sulphide precipitate cadmium sulphide from solutions of cadmium salts containing a slight amount of free acid? Recall the behavior of zinc salts in the presence of the same reagents (?).

Test the solubility of cadmium sulphide in concentrated nitric acid (?). Equation? In ammonium sulphide (?).

(*e*) To a solution of cadmium chloride add a solution of potassium cyanide (Care! Poison!), drop by drop. Observe the precipitation of cadmium cyanide, $Cd(CN)_2$. Equation? Add an excess of the precipitant (?). The soluble complex salt formed is $K_2.Cd(CN)_4$. Equation? Is the cadmium ion present in the solution, theoretically? (See discussion of "double" and "complex" salts under Exp. XVII, "Copper".) Confirm or disprove your conclusions by passing hydrogen sulphide into the above solution. Results? Ionic equations? Is cadmium sulphide soluble in potassium cyanide?

(*f*) What is the color and valence of the cadmium ion?

(*g*) State the tests by which you could distinguish between the salts of zinc and cadmium. Apply to the assistant for an "unknown" solution. Ascertain if the solution contains one or both of the above metals. Make a complete report of your procedure.

MERCURY, Hg.

At. Wt. 200.0 Sp. Gr. 13.59.

Experiment I.—Properties of Mercury.

(*a*) Tabulate the most obvious physical properties of mercury. What particular property does it possess which makes it unique among metals?

(*b*) Does mercury tarnish when exposed to the air?

(*c*) Enumerate those properties of mercury in virtue of which it appeals to you as a metal.

(*d*) Is the molecule of mercury monatomic or diatomic?

(*e*) State some of the uses of mercury. What are *amalgams?*

Experiment II.—Preparation of Mercury by Roasting Cinnabar.

Place a small piece of cinnabar (HgS) in a glass tube open at both ends; clamp the tube in an inclined position so as to permit a free draught of air through it. Heat the tube strongly with the Bunsen flame. Results? Identify the fumes (?). Equation?

Experiment III.—Properties of the Salts of Mercury.

Examine the different salts of mercury (end shelf), noting the obvious physical properties. Heat a small quantity of a mercury salt in a test tube. Result? This property of volatilizing unchanged, giving sublimates of the same compound, is characteristic of many mercury compounds. Give the name, formula and color of each salt. How many series of mercury salts do you find? Tabulate the foregoing data.

Give the formula and use of each of the following substances: *calomel, corrosive sublimate, vermillion.*

Experiment IV.—Formation of Mercurous Nitrate from Dilute Nitric Acid and Mercury.

By means of a glass pipette take two or three drops of mercury from the supply-bottle, place the mercury in a test tube or beaker, and add 15 $cm.^3$ of dilute nitric acid (1 to 1). Allow the action to continue for about an hour (heating gently will hasten the action). An excess of mercury must always be present. Continued stirring will cause crystallization of the *mercurous* nitrate which is formed in the solution under the above conditions. Dissolve the crystals in distilled water which has been made slightly acid by the addition of a few drops of nitric acid. Filter the solution, and reserve the filtrate for use in those experiments in which mercurous nitrate is demanded. Equation? What is the valence of mercury in mercurous nitrate?

Experiment V.—Formation of Mercuric Nitrate from Concentrated Nitric Acid and Mercury.

Boil 10 $cm.^3$ of mercurous nitrate or two or three globules of mercury with an excess of strong nitric acid. Continue the boiling until all of the mercury has disappeared, evaporate nearly to dryness upon a steam bath, add a few drops of nitric acid, and continue the evaporating until the reddish-brown fumes cease to be liberated. The residue is *mercuric* nitrate. Prepare a solution of the salt according to the directions given in the preceding experiment. Reserve the solution for experiments.

Experiment VI.—Precipitation of Mercurous Iodide and Mercuric Iodide.

(*a*) Add a solution of potassium iodide drop by drop to a dilute solution of mercurous nitrate. Result? Equation? What is the effect when an excess of the precipitant is added?

(*b*) Repeat (*a*) using mercuric nitrate instead of mercurous nitrate. Observe the precipitation of the yellow variety of mercuric iodide, which in a few minutes change into the red variety. The conversion into the red form is greatly hastened by light. Add an excess of the solution of potassium iodide. Result? What complex ion is formed? Equation?

Note.—When the red iodide of mercury is heated above 126° it is converted into the yellow crystalline variety of mercuric iodide which if kept in the cold, changes slowly into the red. If the yellow variety is scratched or rubbed, it is converted at once into the red crystalline form. The red variety is stable at temperatures below 126°, and the yellow, above 126°. This is the transition temperature which separates the two regions of stability. Substances like sulphur and mercuric iodide which can change in two directions–i.e., have two regions of stability–are said to possess the property of "*enantiotropy*."*

Experiment VII.—Analytical Reactions of Mercury Salts.

(*a*) Heat a small quantity of a salt of mercury with an equal amount of anhydrous sodium carbonate in a dry test tube. Result?

(*b*) Recall or repeat Exp. XI (*d*) "Electrolysis and Electrical Equivalents."

Note.—To separate portions of a dilute solution of *mercurous* nitrate add the following reagents. Repeat each experiment using a dilute solution of any *mercuric* salt. Compare and tabulate the results.

(*c*) Test with litmus paper (?). Explain.

(d) A solution of sodium hydroxide (?). Equations?

(*e*) Ammonium hydroxide (?). Equations?

(*f*) Dilute hydrochloric acid (?). If a precipitate is formed, filter and treat the precipitate upon the filter paper with ammonium hydroxide. Equations?

Note.—The compound formed by the action of the ammonium hydroxide is *mercurous chloramide*, $NH_2.Hg_2.Cl$. A compound formed by the action of ammonium hydroxide on mercuric chloride is known as *mercuric chloramide*, $NH_2.Hg.Cl$.

(*g*) Hydrogen sulphide (?). If a precipitate is formed, ascertain its solubility in strong nitric acid. Equation?

(*h*) Stannous chloride (?). Use an excess of the reagent and warm gently (?). Equations?

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* Ostwald—Principles of Inorganic Chemistry.

(*i*) Compare the properties of the monomercurion, Hg′, and the dimercurion, Hg″.

(*j*) State how a solution of a mercurous compound can be distinguished from a solution of a mercuric salt.

How could you separate the metals from a solution containing the salts of zinc, cadmium and mercury? Make a brief coherent report of the method of procedure.

PROBLEMS.

1. The atomic weight of mercury is 200.0. If the vapor density of mercury is 100, how many atoms does the molecule contain?

2. 10 grams of zinc will liberate from sulphuric acid how many cm.^{3} of hydrogen at 0° C. and 760 mm.? At 20° C., and 730 mm.?

3. Calculate the percentage composition of cadmium sulphide.

CHAPTER XXVIII.

THE ELEMENTS OF GROUP III.

Family M.		
(Scandium,	Sc.	44.)
(Yttrium,	Y.	89.0)
(Lanthanum,	La.	138.9)
(Ytterbium,	Yb.	173.0)

Family m.		
Boron,	B.	11.0
Aluminum,	Al.	27.1
(Gallium,	Ga.	70.0)
(Indium,	In.	115.)
Thallium,	Tl.	204.1

Scandium, yttrium, lanthanum and **ytterbium,** like certain other elements of the following groups, are generally known as *rare earth metals.* **Cerium** (Ce.; At. Wt.140.2), **praseodymium** (Pr.; At. Wt. 140.5), **neodymium** (Nd.; At. Wt. 143.6), **samarium** (Sa.; At. Wt. 150.3), **gadolinium** (Gd.; At. Wt. 156), and **erbium** (Er.; At. Wt. 166) are usually included amongst the metals of the rare earths. They have been given this generic name because they are found only in small amounts in a few rare earthy minerals, such as *orthite*, *euxenite*, *cerite*, *gadolinite* and *monazite*. Very few of these metals have been isolated in pure elementary form, but many of their salts have been prepared. The latter, however, are so similar in behavior that separation is exceedingly difficult.

The study and isolation of the elements of this group is attended by much difficulty. This is well illustrated by the history of the isolation of the compounds of the elements of praseodymium and neodymium. In 1839, Mosander prepared from the mineral *yttria*, certain oxides, among which there was one which he regarded as a compound of a new elementary substance, to which the name *didymium* was eventually given. Nearly sixty years elapsed before the elementary character of didymium was questioned. The comparatively recent researches of Auer von Welsbach have shown, however, that didymium is a mixture of the two elements, praseodymium and neodymium. The salts of praseodymium are light green while the neodymium salts possess a rose-violet color.

The properties of these elements are similar to those of aluminum, showing the same gradations as were found in preceding groups, with increase of atomic weights; that is, the free metals possessing the greater combining weights are the more readily oxidized and their respective bases are stronger. In their compounds the metals are usually trivalent. The oxides and hydroxides are insoluble in water, and the chlorides, nitrates and sulphates are soluble. The nitrates are decomposed by heat. "Many of these elements give a very complicated spectrum on allowing the electric spark to pass between carbon points moistened with solutions of their salts. Since, under given conditions, each element possesses a perfectly definite spectrum, it can be seen whether the spectrum changes by partial separations. Where this is the case, we are certainly dealing with a mixture. The higher members also exhibit *absorption spectra*, some of them also *emission spectra*."

Several of the metals of this group have atomic weights so near to lanthanum that it seems impossible at present to accommodate them in the periodic table. Ostwald,* in discussing the probable position of lanthanum in the table, says: "This signifies that there exist at this point not *one* element, but a number of elements which are all very close to one another, and have therefore an almost equal claim to this position. This is an occurrence of numerous small planetary bodies at a point of the solar system where, by analogy, one would have expected a large planet."

Scandium, which was discovered in 1879 by Nilson and Cleve, is of particular interest to us because its existence was suggested in 1869 by Mendeléeff who, from considerations based upon the periodic table, predicted its atomic weight and many of its physical and chemical properties. Mendeléeff had given the name of *eka-boron* to the element.

Eka-boron (Predicted 1869).	**Scandium (Discovered 1879).**
Atomic weight, about 44.	Atomic weight, 44.1.
Oxide, Eb_2O_3, soluble in acids, analogous to Al_2O_3, but more basic; insoluble in alkalies.	Oxide, Sc_2O_3, soluble in strong acids, analogous to Al_2O_3, but much more basic; insoluble in alkalies.
Salts colorless and give gelatinous precipitates with NaOH or Na_2CO_3.	Salts colorless and give gelatinous precipitates with NaOH or Na_2CO_3.
Sulphate, $Eb_2(SO_4)_3$, will form a double salt with K_2SO_4, not isomorphous with the alums.	Sulphate, $Sc_2(SO_4)_3$, forms a double salt with K_2SO_4, which is not isomorphous with the alums.

Eka-aluminum (Predicted 1871).	**Gallium (Discovered 1875).**
Atomic weight, about 69.	Atomic weight, 69.9.
Will have a low melting-point.	Melting-point, 30.2°.
Specific gravity, about 5.9.	Specific gravity, 5.93.
Will not be acted upon by the air.	Slightly oxidized at red heat.
Will decompose water at red heat.	Decomposes water at high temperature.
Will give an oxide, El_2O_3.	Gallium oxide, Ga_2O_3.
Will give a chloride, El_2O_6.	Gallium chloride, Ga_2Cl_6.
Will give a sulphate, $El_2(SO_4)_3$.	Gallium sulphate, $Ga_2(SO_4)_3$.
Will form a potassium alum, etc.	Forms a well-defined alum.

*Principles of Inorganic Chemistry.

With the exception of boron, aluminum and thallium, the members of Family III. are among the rarest of the elements. Gallium, indium and thallium were discovered by means of the spectroscope; **gallium** takes its name from the country (France) in which it was discovered by Lecoq. de Boisbaudrau, in 1875; **indium,** by Reich and Richter in 1863, received its name on account of two characteristic lines in the indigo-blue part of the spectrum; and **thallium,** by Crookes in 1861, owes its name to the fact that there is a prominent green line in its spectrum (Gk. θαλλδζ, a green twig). These metals occur in exceedingly small quantities as impurities in zinc blends. They are moderately heavy, similar to one another in most properties, and possess specific gravities and melting points which vary in the order of their atomic weights.

Gallium is a lustrous gray metal which possesses the extremely low fusing-point of 30.2° C. It is oxidized superficially when heated to high temperatures in the air, and is acted upon by strong acids and strong basic hydroxides. **Indium** is a soft white metal which melts at 176°. It burns with a violet flame when heated in the air, and is acted upon by strong acids. **Thallium** is a soft grayish-white metal which oxidizes at ordinary temperature in moist air. It melts at 290°. Sulphuric acid and nitric acid act upon thallium, but hydrochloric acid acts upon it only superficially as the insoluble thallous chloride which forms upon the surface protects the metal.

The hydroxides of these three elements are weak bases. Gallium hydroxide and indium hydroxide may also interact with strong basic hydroxides, but thallium hydroxide shows no such acid properties. Gallium functions both as a bivalent and a trivalent element; indium, as a univalent, bivalent and trivalent element, and thallium, as a univalent and a trivalent element.

Boron is the only non-metal of the group, all the others exhibit well marked basic properties. The oxide, B_2O_3, of boron is acidic. (See Chapter XXII).

Aluminum does not occur native, but its oxides and silicates are found widely distributed. It is prepared by the electrolysis of oxide of aluminum dissolved in cryolite. Aluminum is a silver-white metal, very ductile and malleable, a good conductor of electricity, and melts at 657°. It does not tarnish and is practically without action upon water. It is scarcely acted upon by nitric acid, but readily dissolves in hydrochloric acid and in strong solutions of the caustic alkalies with liberation of hydrogen.

Aluminum functions as a trivalent element in its compounds. It is a highly electro-positive element, and in consequence of its great affinity for oxygen, aluminum displaces all metals save magnesium from their oxides. The extreme readiness with which aluminum is able to effect such reduction when the reaction is once started by heat and the exceedingly high temperature which is reached by the action have led to some very useful applications. The heat of reaction between powdered aluminum and ferric oxide has found useful application in the "*Gold-*

schmidt process" for welding iron and steel. The very high temperature, 2500°–3000°, produced by the reaction is sufficient to melt both the iron and the oxide of aluminum. As the products of the action are not miscible, they separate into two layers. The sulphides are reduced just as readily. This furnishes a simple method for the preparation of pure specimens of the metals whose oxides and sulphides are reduced with difficulty. Goldschmidt, the inventor, has given to these processes the general name of "*aluminothermy*." Mixtures of the metallic oxides and granulated aluminum have been placed on the market under the name of "*thermit*."

The hydroxide of aluminum is feebly acidic as well as basic, and therefore forms two classes of compounds of the types Na_3AlO_3 and $AlCl_3$. The general name of *aluminates* is given to the first class. Both series of salts are hydrolyzed by water, which is to be expected.

Aluminum has a wide range of uses, although the marked influence of traces of impurities has limited its application more than was anticipated originally. It is used for making aluminum bronze, magnalium, flash-light powders, paint, cables for conducting electricity, foil, various ornamental articles and cooking utensils.

The compounds of aluminum are of equal importance. *Ruby*, *corundum* and *sapphire* are nearly pure oxides of aluminum. *Emery* is a mixture of corundum and iron. *Clay*, an impure silicate of aluminum, is used in the manufacture of bricks and earthenware. *Kaolin*, nearly pure aluminum silicate, is used in the manufacture of porcelain and china. *Hydraulic cement* (hardens under water) is made by heating a mixture of limestone and clay to incipient fusion.

BORON, B.

At. Wt. 11.0 Sp. Gr. 2.5.
(See Chapter XXII).

ALUMINUM, Al.

At. Wt. 27.1 Sp. Gr. 2.58.

Experiment I.—Properties of Aluminum.

(*a*) Examine specimens of aluminum in the forms of ingot, wire and powder. Introduce a piece of the wire into the Bunsen flame in order to determine whether aluminum is a conductor of heat (?). Does the wire melt in the flame (use tongs)? Try the blast-lamp (?). What is the melting point of the metal? Does it tarnish in the air?

(*b*) Solubility in acids. Try the action of the powdered or granulated metal on the following reagents: hydrochloric acid (?), nitric acid (?), and sulphuric acid (?). Account for results. Test the gas, if any is liberated (?). Equations?

(*c*) Solubility in the caustic alkalies. Add about 5 cm.^{3} of a concentrated solution of sodium hydroxide or potassium hydroxide to 1 to 2 cm.^{3} of granulated aluminum, and warm gently (?). Identify the gas evolved (?). Add more of the hydroxide if necessary. The solution contains *sodium aluminate*, Na_3AlO_3. Ionic equation? Does the acidic or basic properties of the aluminum hydroxide predominate in this reaction? Your reasons? To prove that aluminum has gone into solution, neutralize the product of the above reaction carefully with dilute hydrochloric acid. Result? Equation? Are the properties of the aluminum revealed by this reaction? Explain.

(*d*) Tabulate the properties of aluminum. Should commercial "lyes" (alkalies) be warmed in cooking utensils made of aluminum? Why?

(*e*) Enumerate some of the uses of aluminum.

Experiment II.—Reduction of Metallic Oxides by Use of Aluminum. The Goldschmidt Process. "Thermit."

Thoroughly mix small quantities of iron oxide and granulated aluminum. Place the mixture on an iron plate or a piece of tile, and ignite it by means of a piece of magnesium ribbon (?). Examine the fused mass for globules of iron. If the above mixture does not ignite readily, procure a small quantity of commercial mixture known as "thermit iron" (iron oxide and aluminum) and ignite it after receiving instructions from the assistant. Account for the results. Equation?

Experiment III.—Salts of Aluminum.

Examine the various aluminum salts found in the laboratory. Record the name, formula and color of each salt. What is *ultramarine*, its formula, color and use?

Experiment IV.—Preparation of the Compound Salt, Potassium-Aluminum Sulphate. Alums.

(*a*) Prepare hot saturated solutions of potassium sulphate and aluminum sulphate—25 cm.^{3} of each solution will be sufficient. Mix the two solutions in a small beaker or crystallizing dish so that the resulting solution contains the weights of the two salts in a proportion approximating the ratio of their molecular weights (10 grams of $Al_2(SO_4)_3.18H_2O$ and 3 grams of K_2SO_4 in 200 cm.^{3} of distilled water. Concentrate to 100 cm.^{3} Cool.) The compound salt, potassium-aluminum sulphate, K_2SO_4, $Al_2(SO_4)_3.24H_2O$, crystallizes on standing (it may be necessary to allow it to stand for several days). What is the form of the crystals?

(*b*) Repeat (*a*), using ammonium sulphate instead of potassium sulphate. Result? Compare the forms of the crystals (?).

(*c*) What is an *alum?* State some of the uses of alums. Notice the composition of the various alums, a list of which is appended. All of these alums crystallize in the same form and possess the same fundamental chemical poperties.

$Na_2SO_4 . Al_2(SO_4)_3 . 24H_2O$,	Sodium alum.
$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$,	Potassium alum.
$(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O$,	Ammonium alum.

Alums are also formed by substituting iron, chromium and manganese for aluminum.

$K_2SO_4 . Fe_2 (SO_4)_3 . 24H_2O$,	Iron alum.
$K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$,	"Chrome" alum.
$K_2SO_4 . Mn_2(SO_4)_3 . 24H_2O$,	Manganese alum.

Experiment V.—Analytical Reactions of Aluminum Salts.

(*a*) Heat a small quantity of an aluminum salt (use alum) on a piece of charcoal in the oxidizing flame (?), moisten with a few drops of a cobalt nitrate solution, and heat again. Account for the blue color of the product.

(*b*) Test a solution of the chloride or sulphate of aluminum with litmus paper (?). Explain.

(*c*) To 10 cm.^{3} of an aluminum sulphate solution add a small quantity of a solution of sodium hydroxide. Filter off the precipitate, and suspend it in water. Divide the mixture into two portions. To one portion add hydrochloric acid (?). Equations? To the second portion add a slight excess of the sodium hydroxide solution (?). Now add an excess of a solution of ammonium chloride (?). Account for the re-precipitation of aluminum hydroxide. Equations?

(*d*) Add a sodium carbonate solution to a solution of aluminum sulphate (?). Filter off the precipitate, and wash it until free from sodium carbonate. Test the precipitate with hydrochloric acid. Is it soluble and is carbon dioxide evolved. Explain. Equations?

(*e*) Add ammonium sulphide to a solution of an aluminum salt. Result? Filter, and wash the precipitate until it is free from the precipitant, i.e., is odorless. Remove the precipitate to a test tube, and add hydrochloric acid (?). Is hydrogen sulphide evolved? Was the precipitate a sulphide?

The hydroxide and not the sulphide was formed in the first reaction as the sulphide cannot exist in the presence of water. Explain. Express the precipitation of aluminum hydroxide by ammonium sulphide by ionic equations.

(*f*) Mordants. (1) To 1 cm.^{3} of a cochineal solution add 5 or 6 cm.^{3} of a solution of aluminum sulphate, then add ammonium hydroxide. Shake vigorously and filter. Locate the coloring matter (?). Does water remove it easily?

(2) Immerse a strip of white muslin in a strong solution of aluminum sulphate. When the muslin becomes saturated, transfer it to a hot solution of cochineal which has been made strongly alkaline with ammonium hydroxide. What are *mordants?* State the purpose of the use of the ammonium hydroxide in conjunction with the aluminum sulphate.

THALLIUM, Tl.

At. Wt. 214.1 Sp. Gr. 11.8.

Experiment I.—Properties of Thallium.

Examine a specimen of the metal (?). It tarnishes on exposure to air with the formation of black thallous oxide. Has the specimen undergone oxidation?

In the univalent condition its properties suggest those of sodium and silver, while trivalent thallium in its compounds resembles aluminum; for example, thallic salts are hydrolyzed by water.

Experiment II.—Salts of Thallium.

Examine those compounds of the metal which are found on the end shelf. Observe the name, formula and color of each salt. How many well-defined series of thallium compounds do you find? What is the valence of thallium in each series? Tabulate data.

PROBLEMS.

1. Calculate the amount of alumnia, Al_2O_3, which can be prepared from 1000 grams of bauxite, $Al_2O(OH)_4$.

$$Al_2O(OH)_4 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2 + 2H_2O,$$
$$2NaAlO_2 + CO_2 + 3H_2O \rightarrow N_2CO_3 + 2Al(OH)_3.$$
$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O.$$

CHAPTER XXIX.

THE ELEMENTS OF GROUP IV.

Family M.			Family m.		
(Titanium,	Ti.	48.1	Carbon,	C.	12.00
(Zirconium,	Zr.	90.6	Silicon,	Si.	28.4
(Cerium,	Ce.	140.25	(Germanium,	Gr.	72.5
(Thorium,	Th.	232.5	Tin,	Sn.	119.0
			Lead,	Pb.	206.9

The four rare elements, titanium, zirconium, cerium and thorium, compose Family M of Group IV.

Titanium as the constituent of several rare minerals occurs chiefly in the form of the crystalline titanium oxide, of which there are several native varieties, known as *rutile*, *anatase* and *brookite*. It is exceedingly difficult to prepare the metal in the pure form, owing to the fact that it combines readily with nitrogen, forming a nitride. **Zirconium** is found in the rare silicate, $ZrSiO_4$, in the mineral *zircon*. This element resembles boron in that it occurs in several allotropic varieties: an amorphous form, a black powder, a graphitic form, and the crystalline form, hard steel-gray *lamellæ*. The amorphous form burns in the air when heated gently, but the crystalline varieties require the high temperature of the oxyhydrogen flame for its ignition. Zirconium dioxide (zirconia), ZrO_2, which emits a white and brilliant light when heated, is used as a constituent of the mantles of the Welsbach lights. **Cerium** occurs chiefly in the two rare minerals, *cerite* and *orthite*. The metal as obtained by electrolysis is steel-gray, lustrous and malleable. It is stable in the air at ordinary temperatures, but possesses the peculiar property of undergoing oxidation with incandescence when heated. In virtue of this latter property, cerium has recently become of much technical importance in the manufacture of the Welsbach mantle. It has been suggested[*] that "the effectiveness of cerium dioxide, CeO_2, as a constituent of the Welsbach mantle in intensifying the light emitted may depend upon the facility with which it is reduced and reoxidized, thereby acting as a catalyzer to cause rapid combustion and high temperature in the flame." **Thorium**, which until comparatively recently was obtained almost solely from *thorite* (a silicate), is now obtained from the mineral *monazite* which is found in abundance in North Carolina. Its metallic properties are very similar to those of cerium. The dioxide of thorium is the chief constituent of the Welsbach mantles, which are usually prepared by moistening a cotton web with a solution containing thorium

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[*] Gooch and Walker—Outlines of Inorganic Chemistry.

nitrate and one per cent. of cerium nitrate, then drying and heating it. The web (organic material) burns and the thoria and ceria remain as a white coherent frame-work. The mantle is made ready for use by heating it in a Bunsen flame produced under pressure. The material of the mantle contracts appreciably as the result of this last operation.

Although the exact rôle of the ceria is not known, yet it is a fact that pure thoria makes a poorly luminous mantle. Ostwald* says: "The cause of this influence (referring to the luminous properties of the mantle when small quantities of certain other substances are mixed with the thoria) has not yet been established quite free from doubt, but the most probable view is that the addition (of the ceria) effects a catalytic acceleration of the combustion of the mixture of coal-gas and air in direct contact with the skeleton of thoria. Besides this, the optical properties of thoria appear to be of importance."

The compounds of thorium are radio-active; i.e., they possess the power of continually emitting certain "influences," sometimes called the "Becquerel rays" and "emanations" which possess the property of effecting a change in the electrical properties of the air. Certain of these "influences" are able to penetrate solid substances and affect a photographic plate. The student is referred to reference works on this subject of radio activity.†

All the metals of this family are quadrivalent.

The elements of Family m. have been divided into two series (see Chapter XX); a primary series embracing carbon and silicon, and a secondary series composed of the elements, germanium, tin and lead. The primary series has been considered previously.

The elements of the secondary series are silver-white, lustrous, malleable metals which are practically unaffected by air or water. The metals are fusible and volatile at high temperatures. They possess high specific gravities which increase as the atomic weights increase.

The rare element **germanium** (Mendeléeff's eka-silicon) forms a sort of link between the elements of the primary series and those of the secondary series. It is both metallic and non-metallic; its oxide combines with acids, but it also unites with alkaline hydroxides. Both **tin** and **lead** which resemble each other, especially in their physical properties, show similar basic and acidic relations in their respective compounds; i.e., their oxides and hydroxides combine with strong acids to form salts in which tin and lead are positive ions, while with the caustic alkalies they form compounds, known respectively as *stannates* of the type, $NaSnO_2$, and *plumbites* of the type, Na_2PbO_2, in which the metals are in the negative ions. Each element of the series forms compounds of the types *stannous chloride* ($SnCl_2$) and *stannic chloride* ($SnCl_4$), in which the metals function, respectively, as bivalent and quadrivalent

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* Prin. of Inorg. Chem.

† Rutherford—Radioactivity; Arrhenius—Theories of Chemistry; Fournier—The Electron Theory.

elements. Lead, however, manifests a greater tendency to react at the state of lower valency. This is not an exception, but rather a rule that the heavier metals of a group tend to react at the lower valency.

The compounds of these three elements, many of which are insoluble, are but slightly hydrolyzed by water and generally stable.

The chief ore of **tin** is tin-stone, or *cassiterite*, SnO_2, the greater portion of which (fully 80 per cent.) is supplied by Cornwall and the East Indies. The metallurgy of tin consists of four processes, namely, (1) crushing or pulverizing the ore, (2) calcining, (3) washing, (4) smelting or reducing. After the ore has been crushed finely and washed to free it from earthy matter, it is calcined in a reverberatory furnace. The latter operation is for the purpose of oxidizing the sulphides of iron and copper and to drive off the arsenic. The sulphur and arsenic are led into condensing flues where the arsenic deposits are collected. The calcined ore is now washed to eliminate the oxide of iron and the sulphate of copper, and then reduced with powdered anthracite coal in a reverberatory furnace. The tin obtained by the foregoing process is further purified by remelting at a gentle heat, the pure and more readily fusible tin being allowed to flow away from the residue and alloys of other metals.

The crystalline character of the metal may be observed by pouring warm dilute *aqua regia* over the surface of a piece of block-tin or a sheet of tinned iron. The surface of the metal after such treatment exhibits a beautiful crystalline appearance. Again, when a bar of tin is bent a peculiar crackling sound (tin cry) is produced. It has been observed also that the metal becomes perceptibly hot at the place of flexure. It has been suggested that the cause of these phenomena may be due to the friction of the crystals upon one another. When ordinary tin, which has a specific gravity of 7.3, is exposed to the prolonged influence of low temperature, it changes to a gray pulverulent variety of specific gravity 5.8. The transition temperature is 20°, and ordinary tin is in a metastable condition below this temperature. Tin is not tarnished by air or water at ordinary temperatures, but when heated above the melting-point it burns with a brilliant white light, forming white clouds of stannic, SnO_2. At red heat tin decomposes steam with a liberation of hydrogen. Hydrochloric acid and tin interact with the evolution of hydrogen and the formation of stannous chloride; when strong sulphuric acid is heated with tin, stannous sulphates and sulphur dioxide are formed; cold dilute nitric acid yields stannous nitrate and ammonia, while concentrated nitric acid gives stannic nitrate, which is hydrolyzed by water with the formation of metastannic acid $(H_2SnO_3)_5$. The caustic alkalies attack tin, giving hydrogen and a metastannate, such as Na_2SnO_3. Tin forms alloys with lead, copper, antimony, bismuth and mercury. Among the more familiar of these alloys are *bronze*, *soft solder* (50 per cent. lead), *pewter* (25 per cent. lead), *Britannia metal* (10 per cent. antimony and a small quantity of copper), and *fusible alloys* (bismuth, tin, cadmium and sometimes lead). Tin is also used as a protective covering on other metals on account of the difficulty with which it is attacked by many corroding substances. *Tin-plate* is made by dipping sheet iron into molten tin. Vessels made of copper are also frequently covered. Ordinary brass pins are made of brass wire coated with tin. The metal finds many other uses in the arts.

Lead is obtained almost wholly from the ore, *galena* PbS. The metallurgical processes by which lead is obtained from its ores are similar to those described for the reduction of sulphides. The metal is refined by electrolytic methods. It is a grayish-white metal, soft and tough. It melts at about 330°, and vaporizes at 1700°. Under suitable conditions it crystallizes, the crystals having the octahedral form. When warm, it may be formed into pipes by hydraulic pressure. It is a poor conductor of electricity. Lead is oxidized but superficially by the air, becoming covered with a film of a dark-colored oxide, which is probably the suboxide Pb_2O, the composition of the final covering being that of a basic carbonate; when heated, the metal passes through several stages of oxidation with the formation of no less than five distinct oxides. Pure water does not act upon lead, but hard water covers it with a coating composed largely of the sulphate and the carbonate. As these salts are insoluble, they protect the metal and prevent contamination of the water with poisonous lead compounds. Water holding air in solution attacks lead, forming the slightly soluble hydroxide and the carbonate. The latter is appreciably soluble in water containing carbon dioxide. The use of lead pipes for conducting water may become a source of danger, as rain water especially, owing to the presence of oxygen and carbon dioxide, is likely to exert a solvent action upon the pipes. The lead compounds taken continuously into the system in small quantities act as a cumulative poison. Hydrochloric acid acts upon the metal slowly with an evolution of hydrogen. Concentrated sulphuric acid has but little affect upon it; dilute sulphuric acid slowly interacts with it, forming the insoluble lead sulphate and sulphur dioxide. Nitric acid attacks it, giving lead nitrate and oxides of nitrogen. The action of the caustic alkalies upon lead has been mentioned previously.

The uses of lead are numerous. It forms useful alloys with tin, antimony, bismuth, copper and zinc. *Type-metal* usually contains lead and antimony and sometimes tin. On account of the resistance of lead to the action of air and water and many other substances, it is employed in making various kinds of vessels and lead pipes for carrying water. *Shot-metal* is an alloy composed of about 99.5 per cent. of lead and 0.5 per cent. of arsenic. "In the process of making *shot* the lead is melted in a cast-iron pan, and after the addition of a sufficient amount of lead arsenide to form an alloy containing from 0.8 to 0.9 per cent. of arsenic, the molten alloy is poured into a perforated iron basin at the top of a high *tower*, and allowed to fall into a dilute solution of sodium sulphide. The presence of arsenic makes the drops of molten alloy very fluid, so that they assume a spherical form in their passage to the bottom of the tower. The effect of the sodium sulphide is to coat the shot with a thin layer of lead sulphide which prevents superficial oxidation when the shot are removed from the water. Shot are sometimes made by allowing the molten metal to fall through an ascending air current or by pouring it in a thin stream upon a rapidly revolving disk, when the centrifugal action divides the metal into drops, which are thrown against a surrounding screen."*

The following table gives a general view of the physical and chemical properties of the metals of this series:

	Germanium.	Tin.	Lead.
Atomic weight,	72.5	119.0	206.9
Specific gravity,	5.47	7.3	11.37
Melting-point,	900°	231°	330°
Volatilizes,	1350°	1500° (?)	1700°
Oxides,	GeO; GeO_2,	SnO; SnO_2,	Pb_2O; PbO; Pb_2O_3; PbO_2; Pb_3O_4.
Chlorides,	$GeCl_2$; $GeCl_4$,	$SnCl_2$; $SnCl_4$,	$PbCl_2$; $PbCl_4$.
Hydroxides,	$Ge(OH)_2$; $Ge(OH_4$,	$Sn(OH)_2$,$Sn(OH)_4$,	$Pb(OH)_2$.
Sulphides,	GeS; GeS_2	SnS; SnS_2,	Pb_2S; PbS.

GERMANIUM, Ge.

At. Wt. 72.5 Sp. Gr. 7.3.
(See lecture notes and text-book.)

TIN, Sn.

At. Wt. 119.0 Sp. Gr. 7.3.

Experiment I.—Properties of Tin.

(*a*) Examine a specimen of this metal and record its most obvious physical properties. What is its melting point? Is it hard or soft?

(*b*) (Quant.) Determine the specific heat of tin. Secure the directions for procedure from the assistant. Calculate the atomic weight of tin, using 0.054 as its specific heat.

(*c*) Does tin tarnish readily when exposed to the action of the air? Enumerate some of the uses of tin. Name its chief ores.

Experiment II.—(Quant.) Determination of the Equivalent Weight of Tin.

In a crucible which has been previously desiccated and weighed, place an accurately weighed quantity (about 0.5 gram.) of pure granulated tin, and cover the metal with about 10 cm.^{3} of concentrated nitric acid.

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* Gooch and Walker.—Outlines of Inorganic Chemistry.

Carefully apply heat (use a hot iron plate) to the crucible. Identify the reddish-brown fumes. When all of the tin has dissolved and the nitric acid has been entirely expelled, place the crucible on a pipe-stem triangle and heat it with a Bunsen burner. The white product is *stannic oxide*, SnO_2. Equation? Cool, and weigh the crucible and contents. Calculate the chemical equivalent of tin. If the valence of tin in stannic oxide is four, what is its atomic weight?

Experiment III.—Formation of Halides of Tin.

(*a*) Stannous chloride. Treat several small pieces of granulated tin with 10 cm.³ of concentrated hydrochloric acid in a test tube, and warm gently to start the action. After the action has continued for some time, pour off the liquid into another test tube and reserve it for use in those experiments in which stannous chloride, $SnCl_2$, is required. Equation?

(*b*) Stannic chloride. Add 3 cm.³ of concentrated nitric acid and 1 cm.³ of hydrochloric acid to 5 cm.³ of stannous chloride, and heat gently. The solution contains stannic chloride, $SnCl_4$. Dilute with 5 cm.³ of water. Equations?

Experiment IV.—Precipitation of Stannous Hydroxide. Sodium Stannite.

To 5 cm.³ of a dilute solution of stannous chloride add carefully a sodium hyrdoxide solution until precipitation is complete. Equation?

Divide the precipitate into two parts. To one portion add an excess of the sodium hydroxide solution (?) and to the other portion add hydrochloric acid (?). Equations?

Suggest a method for the preparation of stannous oxide, SnO. Equation?

Experiment V.—Precipitation of Stannic Hydroxide (*a*—Stannic Acid). Sodium Stannate.

Repeat Experiment IV substituting stannic chloride for stannous chloride.

What product is obtained by heating stannic hydroxide in a crucible? Equation?

Epperiment VI.—Analytical Reactions.

(*a*) Heat a small piece of tin on charcoal before the blow-pipe (?). Allow a drop of cobalt nitrate to fall upon the incrustation, then heat again (?).

(*b*) Place a piece of zinc or suspend a strip of it in a solution of stannous chloride for ten to fifteen minutes. Result? Equation?

(*c*) Add 1 cm.³ of a solution of mercuric chloride to 4 or 5 cm.³ of stannous chloride solution. Result? The solution now contains stannic chloride, $SnCl_4$. Equation? Warm the mixture and note the changes (?). Equation? Does the stannous chloride act as a reducing or an oxidizing agent? Indicate all of the above changes by "ionic" equations. Repeat the foregoing reaction, using stannic chloride instead of stannous chloride (?). How can you distinguish between stannous and stannic compounds?

(*d*) Add a few drops of stannic chloride to 5 cm.^{3} of dilute hydrochloric acid in a test tube. Now add several pieces of magnesium ribbon to the acid solution. What is evolved? Is it an oxidizing or reducing agent when in the nascent condition? When the magnesium has dissolved, add a small quantity of the mercuric chloride solution. Result? Conclusions? Equations?

(*e*) Pass hydrogen sulphide into 5 cm.^{3} of a solution of stannous chloride containing 1 cm.^{3} of dilute hydrochloric acid. Result? Equation? Is the reaction easily reversible? Give reasons for your answer. Filter and wash the precipitate. Place the latter in an evaporating dish, add 10 cm.^{3} of ammonium polysulphide and warm. Result? Equation? Now add hydrochloric acid to the solution of *ammonium sulphostannate*, $(NH_4)_2SnS_3$. Results? What gas was evolved? Equation?

Repeat the preceding reactions, using stannic chloride (?).

(*f*) There are how many ionic forms of tin? What is the color of the tin ions? Give the valencies of the respective ions.

LEAD, Pb.

At. Wt. 206.9 Sp. Gr. 11.37.

Experiment I.—Properties of Lead.

(*a*) File or scrape off the coating from a piece of lead. Is the metal hard or soft? Color? Does lead tarnish (oxidize) readily in the air? Try to mark on paper with lead (?).

(*b*) Solution tension. Dissolve about 1 gram of lead acetate, $Pb(C_2H_3O_2)_2$, in 20 cm.^{3} of water. Place a strip of sheet zinc or several pieces of granulated zinc in the solution, and set aside for an hour. Result? Ionic equation? Remove the film of lead from the zinc, thoroughly wash the former and reserve it for (*c*).

(*c*) Action of air and water on lead. Spread the finely divided lead from (*b*) on a glass plate, moisten with a very little water, and expose to the action of the air for an hour. Test the water with litmus papers (?). Conclusions? The presence of lead in the water may be detected by shaking a portion of the lead with a small volume of water and passing hydrogen sulphide into the filtrate. A black precipitate (lead sulphide) indicates the presence of lead. Equations?

(*d*) Name the chief ore of lead. What are some of the uses of lead? What is its melting point? What is *pewter?*

Experiment II.—(L. T.) Precipitation of Lead from its Salts by Other Metals. "Lead Tree."

Suspend a bar of zinc in a solution of lead acetate or nitrate. Allow this to stand for several days. The lead will be gradually thrown out of solution (why?) and deposited upon the zinc in arborescent forms, known as the "lead tree." Test the solution for the presence of zinc, as follows: Add sufficient sulphuric acid to precipitate any lead remaining in solution, filter, and to the filtrate add ammonia in excess and ammonium sulphide; the zinc will be precipitated as sulphide. Ionic equations?

Experiment III.—Salts of Lead.

Examine a number of the salts of lead. Give color and formula of each. What is the valency of lead?

Note.—Lead forms five oxides; give the name and formula of each.

Experiment IV.—Precipitation of Lead Hydroxide. Sodium Plumbate.

(*a*) To a solution of lead nitrate add at first slowly and then in excess a sodium hydroxide solution. Describe all of the changes that occur. Ionic equations? Does lead exhibit the properties of both a metal and non-metal? Give reasons for your answer.

(*b*) Repeat (*a*) using ammonium hydroxide.

Experiment V.—Preparation of Lead Salts.

(*a*) Lead nitrate from lead and nitric acid. Treat about a gram of lead in an evaporating dish with 20 cm.^{3} of a mixture (1 to 2) of nitric acid and water. Place the dish on a wire gauze and heat gently until the metal dissolves. Note the accompanying phenomena. Set the solution aside to crystallize by spontaneous evaporation. Result? Equation?

(*b*) Lead nitrate from lead monoxide (*litharge*) and nitric acid. Dissolve 3 to 5 grams of lead monoxide in dilute nitric acid, filter, evaporate the filtrate to the crystallizing point, and cool. Result? Equation?

(*c*) Lead nitrate and lead dioxide from red-lead oxide (*minium*) and nitric acid. Treat about a gram of minium with dilute nitric acid, warm gently, and when the red color of the minium has changed to a brown, dilute with water and filter. Wash the residue (?) and ignite it. Which of the oxides of lead does it resemble most in appearance? Prove the presence of lead in the filtrate by adding slowly an excess of a solution of sodium hydroxide (?). Equations? This behavior of minium suggests what theory as to its constitution?

(*d*) Lead acetate from lead oxide and acetic acid. To 5 grams of lead monoxide add 10 cm.^{3} of acetic acid, then warm gently to increase the speed of the reaction. If the solution is not clear, filter, and evaporate to the crystallizing point, exercising care to avoid charring the salt. Equations? What is "*sugar of lead?*"

Experiment VI.—Precipitation of Lead Carbonate. Basic Lead Carbonate; its Decomposition by Heating.

(*a*) When a solution of ammonium carbonate is added to a solution of lead nitrate, the normal carbonate is formed. (Equations?) If any other alkaline carbonate is used, a *basic lead carbonate* is formed.

(*b*) To 10 cm.³ of a solution of lead nitrate add an excess of sodium carbonate solution (?). Filter, wash and dry the precipitate, separate it from the filter paper, and ignite the white powder in a porcelain crucible. Avoid heating the crucible above dull redness. Observe the color of the residue (?) when hot and cold. Equations? What is "*white lead*"? Its use?

Experiment VII.—Chemical Principles Involved in the Manufacture of "White Lead."

Add a little lead monoxide to 10 cm.³ of a solution of lead acetate; thoroughly shake the mixture; pass carbon dioxide (generator on end shelf) through it until it is white; filter. The precipitate is used as a pigment under the name of "white lead." Equations? What is the effect of hydrogen sulphide upon white lead? Equation?

Experiment VIII.—Analytical Reactions.

(*a*) Heat a small piece of lead on charcoal in the oxidizing flame (blow-pipe). Result? Equation?

(*b*) Test a solution of lead nitrate with litmus paper (?). Interpret the result.

(*c*) Halides of lead. To 2 cm.³ of a solution of lead nitrate add dilute hydrochloric acid until precipitation is complete? Filter, wash the precipitate, and *heat* it with the smallest volume of water which will dissolve it. Cool the solution. Result? Equations?

In what two respects does lead chloride differ from silver chloride? Name the insoluble chlorides.

Treat a cm.³ of lead nitrate solution with a solution of potassium or sodium bromide. Results? Equation? Is the precipitate soluble in hot water? Compare its solubility with that of lead chloride.

Add a solution of potassium iodide to 2 cm.³ of lead nitrate solution. Results? Equation?

How does the solubility of the precipitate compare with the solubility of lead bromide?

(*d*) To 2 cm.³ of lead nitrate solution add dilute sulphuric acid. Result? Equation. What sulphates are insoluble? Give the formula of each.

(*e*) Allow hydrogen sulphide (generator on end shelf) to bubble slowly through 5 cm.³ of a solution of lead nitrate to which has been added four or five drops of dilute nitric acid. Result? Equation? Is the action reversed easily? Give reasons for your answer.

(*f*) Add a dilute solution of potassium chromate to 3 cm.³ of lead nitrate solution. Result? Equation? Is the precipitate soluble in a strong solution of sodium hydroxide? Equation? What is "*chrome yellow*"? Its uses?

(*g*) What is the color of the lead ion? Does it ever form a part of the anion? If so, give an example.

PROBLEMS.

1. Calculate the weight of tin in 1 kg. of cassiterite, SnO_2.

2. What per cent. of lead is contained in galena, PbS?

3. If 50 grams of tin yields 63.55 grams of stannic oxide, what is the atomic weight of tin?

4. An analysis showed that 1 gram of lead monoxide contained 0.0717 gram of oxygen. Calculate the atomic weight of lead.

5. The per cent. of lead in lead chloride is 74.4 and the specific heat of the metal is 0.031. Calculate the atomic weight of lead.

CHAPTER XXX.

ELEMENTS OF GROUP V.

Family M.

(Vanadium, V. 51.2)
(Columbium, Cb. 94.)
(Tantalum, Ta. 181.)

The elements of this family are lustrous gray solids which are very rare and difficult to isolate. Vanadium is the least uncommon. The members of the family are closely related to one another.

Vanadium, which was first isolated by Roscoe in 1867, is found in the complex mineral, *vanadinite*, $Pb_4(PbCl)(VO_4)_3$. It is slowly acted upon by air at ordinary temperatures, but when heated it burns brilliantly, forming the reddish-brown vanadium pentoxide, V_2O_5. This oxide interacts with bases giving *vanadates*. The metal possesses very feeble base-forming properties. Vanadium also combines with nitrogen at red heat to form the yellowish-red vanadium nitride, VN. The following are among the more important of its compounds: V_2O, V_2O_2, V_2O_3, VO_2, V_2O_5, VCl_2, VCl_3, VCl_4, $VOCl_3$, $VOCl_5$, V_2S, V_2S_3, and H_3VO_4. The element is frequently prepared by heating VCl_2 in a stream of hydrogen.

Columbium (niobium) and **tantalum** are found in the rare minerals *columbite*, $(Mn,Fe)(Cb,Ta)_2O_6$, and *tantalite*, $(Fe,Mn)Ta_2O_6$, respectively. These two elements likewise possess feebly base-forming properties. The chief compounds are the *columbates* and *tantalates*. Other compounds are, Cb_2O_2, Cb_2O_4, Cb_2O_5, $CbOCl_3$, $CbCl_3$, $CbCl_5$, H_3CbO_4, Ta_2O_4, Ta_2O_5, $TaCl_5$ and H_3TaO_4.

CHAPTER XXXI.

ELEMENTS OF GROUP VI.

Family M.

Chromium,	Cr.	52.1
(Molybdenum,	Mo.	96.0)
(Tungsten,	W.	184.0)
(Uranium,	U.	238.5)

The elements of this group possess many properties in common. They are hard metals possessing a metallic luster and a high specific gravity. They are attacked by acids, but are not acted upon by air and water at ordinary temperatures. They are readily oxidized or reduced and their corresponding compounds are structurally and chemically similar. Their higher oxides are acid anhydrides, while their lower oxides are basic in character. They form two classes of salts, the "ous" and the "ic"; also two classes of compounds, "ites" and "ates," in which the elements appear in the negative ions.

The maximum valence shown by the elements of this group is VI. Chromium, however, in perchromic acid, $H_2Cr_2O_8$, reaches a valence of VII.

CHROMIUM, Cr.

At. Wt. 52.1 Sp. Gr. 6.92

Chromium does not occur in nature in the uncombined condition, and its natural compounds are neither abundant nor widely distributed. The chief source of chromium is *chrome iron ore*, or *chromate*, $FeCr_2O_4$. It is prepared most conveniently by the "Goldschmidt" process. Chromium prepared by this method is "*passive*" and does not displace hydrogen from hydrochloric acid until it is warmed with the acid. When removed from the acid and left in the air, it changes slowly into the inactive form again. Chromium fuses in the electric arc, but not in the oxyhydrogen flame.

Chromium forms the following oxides and hydroxides: hypothetical chromous oxide, CrO, and chromous hydroxide, $Cr(OH)_2$, which are distinctly basic; chromic oxide, Cr_2O_3, and chromic hydroxide, $Cr(OH)_3$, which are weakly basic; chromic oxyhydroxide, $HCrO_2$, which is acidic; chromium trioxide, Cr_2O_3, a water solution of which is called chromic acid, H_2CrO_4.*

It is obvious that chromium gives four classes of compounds, *chromous* and *chromic salts* which correspond to $Cr(OH)_2$ and $Cr(OH)_3$, and

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* The compound H_2CrO_4 has not been isolated.

chromites and *chromates*, to $HCrO_2$ and H_2CrO_4, respectively. There is also another class, *perchromates*, which correspond to perchromic acid, $H_2Cr_2O_8$.

The chromous salts are not stable in the air owing to the ease with which they pass into the condition of higher oxidation of chromic compounds. All of the chromic salts are hydrolyzed, $CrCl_3$ and $Cr_2(SO_4)_3$ to a small degree, while neither the carbonate nor sulphide is stable in water. (In this respect chromic salts are very similar to corresponding aluminum salts.) The perchromates are unstable at ordinary temperatures.

It is to be noted that those chromium ions of "lower valence, or with the smaller electrical charge, are basic; but as the valence increases, or as the amount of electrical energy which they carry increases, the basic property becomes less and less, and acidic properties begin to manifest themselves."*

Experiments I.—Properties of Chromium.

Examine the metal and note its most obvious physical properties. Does it tarnish in the air?

Experiment II.—Compounds of Chromium.

(*a*) Examine the compounds of chromium (end shelf). Give the color and structural formula of each compound. Record the valence of the chromium atom in each compound, and state whether it behaves as an acid-forming or base-forming element. Tabulate the foregoing data.

(*b*) What is the formula, color and electrical charge of each of the following ions: the dichromate ion and the chromic ion. Hint: Examine solutions of the salts giving these ions (end shelf).

Experiment III.—Preparation of a Chromate.

Mix 5 grams of potassium carbonate with equal amounts of potassium nitrate (supplies oxygen) and potassium hydroxide in an iron crucible (T.O.). Heat the mixture at low temperature until it melts, then stir (use iron rod) in 5 grams of powdered chromite. Heat strongly in the flame of a blast-lamp until further heating produces no more change. Allow the crucible to cool, then dissolve the contents in a little boiling water. Filter. What is the color of the solution? The color is due to the presence of what ion?

$$4(FeO,Cr_2O_3) + 8(K_2O,CO_2) + 7O_2 \rightarrow 8(K_2O,CrO_3) + 2Fe_2O_3 + 8CO_2.$$

Experiment IV.—Formation of a Dichromate from a Chromate.

To 5 cm.^{3} of potassium chromate solution add sulphuric acid, drop by drop, until the yellow color changes to orange. The color is due to the presence of what ion? Evaporate in small beaker to crystallizing point; cool slowly. Note color and shape of crystals.

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* Jones, Elements of Inorganic Chemistry

Interpret the following equations:

$$K_2CrO_4 + H_2CrO_4 \rightarrow K_2Cr_2O_7 + H_2O.$$
$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

Experiment V.—Formation of a Chromate from a Dichromate.

To 5 cm.³ of potassium dichromate solution add enough sodium hydroxide solution to turn the color yellow. The color is due to the presence of what ion? What salt has been formed by the interaction? Equation? Evaporate until a crust forms, then set aside to crystallize. Record color of crystals.

Experiment VI.—Formation of Chromium Trioxide (Chromic Anhydride); its Oxidizing Power. Chromic Acid.*

Prepare about 10 cm.³ of a warm saturated aqueous solution of potassium dichromate in a beaker. Filter the solution if it is not clear. Now add carefully, a drop at a time, an equal volume of concentrated sulphuric acid. Red needle-shaped crystals of chromium trioxide will separate.* Equation? When the mixture has cooled, filter through a plug of glass wool or asbestos (not filter paper). (*Caution: Do not allow the crystals to come in contact with the hand.*) By means of a glass or porcelain spatula remove a few of the crystals and place them upon a piece of filter paper. Account for the result. Treat a few of the crystals in a test tube with a little hydrochloric acid and warm gently.

Identify the gas liberated (Hint: Odor?). Explain. What is the green substance formed which remains in solution?

$$2CrO_3 + 12HCl_3 \rightarrow 2CrCl_3 + 3\overline{Cl_2} + 6H_2O.$$

Pour a drop or two of alcohol upon some of the crystals. The action (oxidation) is so violent that the alcohol frequently takes fire. Try the solubility of some of the crystals in water (?). What is formed? Equation?

The oxidizing power of chromates and dichromates in the presence of an acid is due to the presence of what compound?

Experiment VII.—Formation of Perchromic Acid.

To 5 cm.³ of a solution of potassium chromate add sulphuric acid until the yellow color of the solution changes to orange (avoid large excess of acid), then add hydrogen peroxide. If the procedure has been successful, blue color will be imparted to the solution by the unstable perchromic acid, $H_2Cr_2O_8$.

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* If the solutions are dilute and there is not present a body capable of being oxidized the decomposition is limited to the liberation of chromic acid, $H_2O.Cr\,O_3$.

Note.—The perchromic acid is supposed to be a compound of CrO_3 and H_2O_2.

$$K_2CrO_4 + H_2SO_4 \rightarrow (H_2O.CrO_3) + K_2SO_4.$$
$$\underline{K_2CrO_4 + (H_2O.CrO_3) \rightarrow K_2Cr_2O_7. + H_2O.}$$
$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O,$$
$$K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + 2CrO_3 + H_2O$$
$$2CrO_3 + H_2O_2 \rightarrow H_2Cr_2O_8.$$

The above reaction is used as a delicate test for either hydrogen peroxide or a chromate.

Experiment VIII.—Chromium as a Base-forming Element. Reduction of a Chromate to a Chromic Salt. Chrome Alum.

To a *cold* saturated solution of potassium dichromate acidified with sulphuric acid, add any one of the following reducing agents until the reddish-yellow color has changed to a dark violet: SO_2 (sulphurous acid), $H_2C_2O_4.2H_2O$ (oxalic acid), C_2H_5OH (alcohol).

The solution now contains chromium sulphate, $Cr_2(SO_4)_3$. The color is due to the presence of what ion? Set the solution aside and allow it to evaporate spontaneously. Observe the color and form of the crystals. Compare them with crystals of chrome alum, $K_2SO_4,Cr_2(SO_4)_3.24H_2O$. Your conclusions as to the identity of the crystals? The changes may be represented thus:

$$2CrO_3 + 3SO_2 \rightarrow Cr_2(SO_4)_3,$$
$$K_2Cr_2O_7 + H_2O.SO_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O.$$
$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + (3O) + 4H_2O,$$
$$3C_2H_5OH + (3O) \rightarrow \underset{\text{(Aldehyde)}}{3C_2H_4O} + 3H_2O.$$
$$K_2SO_4 + Cr_2(SO_4)_3 + 24H_2O \rightarrow \underset{\text{Chrome alum.}}{(K_2SO_4,Cr_2(SO_4)_3.24H_2O)}$$

Is chrome alum a double or complex salt? Give reasons for your answer. Does chromium function in this salt as an acid or base-forming element? Potassium chrome alum is the analogue of potassium aluminum sulphate ("alum"). How can a chromate be changed to a dichromate? A dichromate to a chromate? A chromate to a chromic salt?

Experiment IX.—Hydrolytic Decomposition of Chromium Sulphate.

Place 5 cm.³ of a solution of chromium sulphate (chrome alum will do) in a test tube and warm gently. Note the transition from the violet chromic sulphate to the green chromic sulphate. This transition has been attributed to hydrolytic decomposition:

$$2Cr_2(SO_4)_3 + H_2O \rightleftarrows (Cr_4O(SO_4)_4)SO_4 + H_2SO_4.$$

Experiment X.—Formation of Chromyl Chloride. A Test for a Chloride.

In a test tube fitted with a delivery tube warm a mixture of a chloride and potassium dichromate with strong sulphuric acid. Pass the red-brown vapor (chromyl chloride, CrO_2Cl_2) which is disengaged into a second test tube containing a solution of an alkaline hydroxide. The formation of a chromate is indicated by the yellow color which the solution assumes, and may be confirmed by acidifying and adding a lead-nitrate solution. Presence of the chromate is proof of the presence of a *chloride* in the original mixture. As no corresponding bromine and iodine compounds are known, it is obvious that by means of this test it is possible to detect a chloride in the presence of either a bromide or iodide.

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2\overline{CrO_2Cl_2} + 3K_2SO_4 + 3H_2O.$$
$$CrO_2Cl_2 + 4NH_4OH \rightarrow (NH_4)_2CrO_4 + 2NH_4Cl + 2H_2O.$$

Experiment XI.—Formation of Chromic Hydroxide.

To 10 cm.^{3} of a solution of chrome alum add ammonium hydroxide in slight excess. Result? Equation? Wash the precipitate of chromic hydroxide, $Cr(OH)_3$, with hot water; dry and reserve it for the following experiment.

Experiment XII.—Oxidation of a Chromic Compound to a Chromate.

(*a*) Mix a portion of the chromic hydroxide prepared in the foregoing experiment with equal portions of potassium nitrate and sodium carbonate and fuse the mixture in an iron crucible or on a piece of platinum foil. Dissolve the fused mass in water and filter. What is the color of the filtrate? Test it for potassium chromate by acidifying with acetic acid and adding a solution of lead nitrate. Result?

(*b*) To 5 cm.^{3} of a solution of a chromium salt (chrome alum) add sufficient sodium hydroxide to make solution alkaline. How add a large volume of bromine water and heat gently. What is the nature of the change? Lead peroxide and other oxidizing agents may be substituted for the bromine water.

Experiment XIII.—Analytical Reactions.

(*a*) Make a borax bead, touch it with a small quantity of any chromium compound and heat in both the oxidizing and reducing flames. The grass-green color is imparted to the bead by all of the chromium compounds.

(*b*) Reactions of chromates.

1. Recall the action of sulphuric acid on a solution of potassium chromate. Equation?

2. Boil a potassium dichromate solution which has been acidified with dilute acid with 1 cm.^{3} of alcohol. Account for results. Equation?

3. Pass hydrogen sulphide into an acid solution of potassium chromate. Results? Does the hydrogen sulphide act as an oxidizing or reducing agent? Equation?

4. Recall the action of hydrogen peroxide on an acid solution of a chromate. Equation?

5. Add a solution of barium chloride to a potassium chromate solution (?). Equation?

6. Repeat 5, using a potassium dichromate solution. Compare results. Equation?

7. Repeat 5 and 6, using a solution of lead nitrate or lead acetate. Do dichromates precipitate dichromates or chromates when added to a solution of a salt whose chromate is insoluble?

(*c*) Reactions of chromic salts.

1. Recall the effect of boiling a solution of a chromic salt (see Exp. IX). Equation?

2. To a solution of potassium chromium sulphate (chrome alum) add slowly a little of a solution of sodium hydroxide (?); then in excess (?) Equations? Does aluminum hydroxide behave in a manner similar to the chromium hydroxide? Equation? Is the chromium hydroxide reprecipitated when the solution is boiled?

3. Treat a solution of chrome alum with sodium carbonate solution. Account for the precipitation of chromium hydroxide. Ionic equations?

4. Add ammonium sulphide to another portion of the solution of chrome alum. Filter, and wash the precipitate until free from odor. Prove that it is not a sulphide. What other metal fails to form a stable sulphide in the presence of water? Equation?

(*d*) Ions. What ions are yielded by chromates and chromic salts?

MOLYBDENUM, MO.

At. Wt. 96.0 Sp. Gr. 8.6.

Molybdenum is found chiefly in the two uncommon minerals, *molybdenite*, MoS_2, and *wulfenite*, $PbMoO_4$. It is a hard, silver-white metal which is less fusible than platinum. At ordinary temperatures, it remains unchanged in the air, but on heating it oxidizes to molybdenum trioxide, MoO_3. This oxide interacts with the alkalies forming *molybdates* of the type of *sodium molybdate*, $Na_2MoO_4.10H_2O$. Nitric acid precipitates a hydroxide $MoO(OH)_4$ from solutions of these molybdates. This hydroxide gives *molybdic acid*, H_2MoO_4, when heated sufficiently to dry it. When sodium phosphate is added to a solution of ammonium molybdate in nitric acid the yellow pulverulent *ammonium phosphomolybdate*, $(NH_4)_3PO_4.11MoO_3.6H_2O$, is precipitated. This is one of the more familiar of the complex phosphomolybdates. The formulæ of some of the more important compounds of molybdenum are as follows: MoO, Mo_2O_3, MoO_2, MoO_3, $MoCl_2$, $MoCl_3$, $MoCl_4$, $MoCl_5$, MoO_2Cl_2, $MoOCl_4$, MoS_2, MoS_3, Na_2MoO_4, $K_2Mo_3O_{13}.10H_2O$, $Na_2Mo_4O_{13}.6H_2O$.

It is evident that molybdenum possesses valences ranging ordinarily from II to VI.

TUNGSTEN, W.

At. Wt. 184.0 Sp. Gr. 19.1.

Tungsten occurs in the minerals *wolframite*, $3FeWO_4.3MnWO_4$, *scheelite*, $CaWO_4$, and *hübnerite*, $MnWO_4$. The metal possesses properties similar to those of molybdenum. If forms a class of compounds, many of which are analogues of the compounds of the previously mentioned element. The salts corresponding to *tungstic acid*, H_2WO_4, are known as tungstates. The following list contains the formulæ of some of the better known compounds: WO_2, WO_3, WCl_2, WCl_4, WCl_5, WCl_6, $Na_2WO_4.2H_2O$, $Na_2W_4O_{13}.10H_2O$.

The metal is used in the manufacture of *tungsten steel*, a very hard variety of which contains about 5 per cent. of tungsten.

URANIUM, U.

At. Wt. 238.5 Sp. Gr. 18.7.

Uranium is found in the ore *pitchblende*, which contains the mineral *uraninite*, U_3O_8, and several other rare minerals. It is a heavy, silvery-white metal which decomposes water at ordinary temperatures and burns in the air at 175° when in the powdered form. Some of the more important compounds are, *uranous oxide*, UO_2, *uranic anhydride*, UO_3, *uranous chloride*, UCl_4, *uranic* or *uranyl sulphate*, $UO_2SO_4.6H_2O$, *sodium diuranate*, $Na_2O_2O_7$. Many of the uranyl compounds are yellow in color, with green fluorescence. Sodium diuranate is used in making *uranium glass* which shows a yellowish-green fluorescence.

The compounds of uranium are of particular interest because of being the object of much investigation in connection with the phenomena of *radio-activity*. In 1898, Becquerel noticed that all compounds of uranium gave out radiation capable of affecting a photographic plate covered with dark light-proof paper. His observations eventually led to the discovery, by Mme. Curié of the element *radium*. (The student is urged to consult some text-book on the subject of radio-activity, for example, Rutherford,—Radio-activity.)

PROBLEMS.

1. Calculate the percentage composition of (a) lead chromate, $PbCrO_4$, (b) chromite, $FeCr_2O_4$.

2. If 10 grams of chromous chloride, $CrCl_2$, yield 5.75 grams of chlorine, what is the atomic weight of chromium?

3. 10 grams of silver chloride are formed by the interaction of silver nitrate and 3.6865 grams of chromic chloride; what is the atomic weight of chromium?

$$3AgNO_3 + CrCl_3 \rightarrow Cr(NO_3)_3 + 3AgCl.$$

CHAPTER XXXII.

ELEMENTS OF GROUP VII.

Family M.

MANGANESE, Mn.

In the periodic table, according to the present classification, **manganese** stands alone on the left side of the eighth column. The elements of the halogen group occupy the right side. It is both an acid-forming and base-forming element, and probably forms as large a variety of compounds as any element known. This latter property is due to the many degrees of valence which manganese can manifest.

Although manganese occurs native in small amounts associated with iron in meteorites, it is found principally in combination in minerals, some of which are rather widely distributed. The chief source of the metal is *pyrolusite*, MnO_2. Other minerals containing it are: *baunite*, Mn_2O_3, *hausmannite*, Mn_3O_4, the hydrated form, *manganite*, $MnO(OH)$, *manganese spar*, $MnCO_3$, and *manganese blende*, MnS.

Manganese may be obtained by heating the oxides with carbon in an electric furnace or by electrolysis of the fused chloride. It is prepared more conveniently, however, by the "Goldschmidt Process"; i. e., by mixing the oxide with finely divided aluminum and igniting the mixture. The aluminum takes the oxygen and sets free the manganese.

Manganese is a hard, grayish-white, brittle metal of brilliant luster. It is slightly magnetic and fuses at 1900°. It is permanent in dry air, but readily oxidizes superficially on exposure to moist air, and slowly decomposes boiling water with the evolution of hydrogen when the metal is in the finely divided condition. It dissolves readily in dilute acids with the formation of manganous salts. The metal is used as a component of the alloys, *ferro-manganese* (20 to 75 per cent. manganese), and *spiegeleisen* (iron-manganese carbide), which are of use in the metallurgy of Bessemer steel. "*Manganin*" is an alloy of copper, manganese and nickel, containing from eight to ten per cent. of manganese and three to four per cent. of nickel. In the form of wire it is much used in the construction of resistance coils because of its very low resistance temperature coefficient.

Manganese forms five rather well defined sets of compounds which correspond to its series of oxides. The composition of these compounds is as follows:

Manganous,	Manganic,	Manganites,	Manganates,	Permanganates.
MnO	Mn_2O_3	MnO_2	MnO_3	Mn_2O_7
$Mn(OH)_2$	$Mn(OH)_3$	H_2MnO_3	H_2MnO_4	$HMnO_4$
$MnSO_4$	$Mn_2(SO_4)_3$	$CaMnO_3$	K_2MnO_4	$KMnO_4$
$MnCl_2$	($MnCl_3$)	etc.	etc.	etc.
etc.				

The *manganous salts* are *pale pink* in color and are but slightly hydrolyzed. The oxide is green powder and a strong base. The *manganic salts* are *violet* in color and are completely hydrolyzed. Manganese sesquioxide is a weak base. The *manganites* are usually of dark color and are strongly hydrolyzed. Manganese dioxide is a black solid and behaves as an indifferent oxide. The *manganates* are *green* in color and are very easily hydrolyzed, the free acid decomposing and yielding a higher acid ($HMnO_4$) and a lower oxide (MnO_2).

Manganese trioxide is an amorphous red solid soluble in water. It is viewed as the anhydride of manganic acid, H_2MnO_4. The *permanganates* are purplish-red in color and are not hydrolyzed by water. The septoxide of manganese, Mn_2O_7, is an oily, dark liquid which is presumably the anhydride of *permanganic acid*, $HMnO_4$.

Manganese has a valence of II, III, IV, VI and VII. If the existence of manganese tetroxide, MnO_4, is admitted, then the metal has a maximum valence of VIII.

It should be noted that as the valence of manganese increases, its basic nature diminishes, and that it loses all of its basic nature and manifests strong acid properties when in the condition of higher valence.

MANGANESE, Mn.

At. Wt. 55.0 Sp. Gr. 7.2–8.0.

Experiment I.—Note the most obvious physical properties of manganese.

Does it oxidize in the air? What are some of the uses of manganese?

Experiment II.—Compounds of Manganese.

Follow directions given in Experiment II, "Chromium," substituting the word permanganate for the word dichromate.

Experiment III.—Preparation of a Manganate. Oxidation of a Manganate to a Permanganate.

(*a*) Grind in a mortar 5 grams of potassium hydroxide and 2.5 grams of potassium chlorate; transfer the mixture to an iron crucible (T. O.) or a porcelain crucible, and heat until the mixture fuses, then add gradually 5 grams of powdered manganese dioxide while stirring with an iron rod or the reverse end of a file. Maintain the crucible at a red heat for 15 to 20 minutes. Dissolve the green mass (potassium manganate) in a little cold water, then decant the clear liquid away from the residue. What is the color of the solution? This color is due to the presence of what ion?

$$2\,MnO_2 + 6KOH + KClO_3 \rightarrow 3K_2MnO_4 + KCl + 3H_2O.$$

(*b*) Divide the green solution from (*a*) into four parts. Dilute one portion with an equal volume of distilled water, and set aside for several days. It will become purple in color owing to the oxidation of the manganate to the permanganate. Pass carbon dioxide (generator) through one portion of the manganate solution. Result?

$$3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + \underline{MnO_2} + 2K_2CO_3.$$

What is the color of the permanganate ion? Interpret the following equations:

$$K_2MnO_4 + 2H_2O \longrightarrow 2KOH + (H_2MnO_4), \qquad (1)$$

$$\text{or}\quad 2K^{\prime} + MnO^{\prime\prime}_4 + 2H^{\prime} + 2OH^{\prime} \longrightarrow 2K^{\prime} + 2OH^{\prime} + (H_2MnO_4),$$

$$H_2MnO_4 = H_2O,MnO_3,$$

$$3(H_2O,MnO_3) \longrightarrow H_2O,Mn_2O_7 + \underline{MnO_2} + 2H_2O, \qquad (2)$$

$$\text{or}\quad H_2O,Mn_2O_7 = 2HMnO_4$$

$$3H_2MnO_4 \longrightarrow 2HMnO_4 + \underline{MnO_2} + 2H_2O \qquad (3)$$

$$2KOH + 2HMnO_4 \longrightarrow 2KMnO_4 + 2H_2O$$

The partial equations may be summarized:

$$3K_2MnO_4 + 2H_2O \longrightarrow 2KMnO_4 + 4KOH + \underline{MnO_2}$$

The ionic equation:

$$6K^{\prime} + 3MnO^{\prime\prime}_4 + 2H^{\prime} + 2OH^{\prime} \longrightarrow 6K^{\prime} + 2MnO^{\prime}_4 + \underline{MnO_2} + 4OH^{\prime}.$$

What is the difference between the manganate-ion and the permanganate-ion?

Experiment IV.—Oxidizing Power of Manganates and Permanganates.

Note.—Potassium permanganate as well as potassium manganate are powerful oxidizing agents.

(*a*) Manganates. To a warm dilute solution of oxalic acid add an alkaline solution of potassium manganate drop by drop. The oxalic acid is oxidized to carbon dioxide (prove that it is evolved) and water. The manganese is reduced to the bivalent condition with the formation of manganous sulphate, $MnSO_4$.

(*b*) Permanganates.

1. Repeat (*a*) with a solution of potassium permanganate to which has been added an equal volume of dilute sulphuric acid. Result? Equation?

2. To 5 cm.^{3} of sulphurous acid add an acidified solution of potassium permanganate drop by drop. Results? Equation?

3. Add sulphuric acid to a solution of ferrous sulphate, $FeSO_4$, then add potassium permanganate solution drop by drop. The ferrous sulphate is oxidized to ferric sulphate, $Fe_2(SO_4)_3$, and the permanganate is reduced. Explain the color changes. Equation?

4. Add a solution of potassium hydroxide to a potassium permanganate solution. Result? Equation?

5. Recall or again try the action of hydrogen peroxide on an acidified solution of potassium permanganate.

Interpret the following equations:

$$2KMnO_4 + 3H_2SO_4 \rightarrow \underline{K_2SO_4} + 2MnSO_4 + 3H_2O + (5O).$$

$$5C_2H_2O_4 + (5O) \rightarrow 10CO_2 + 5H_2O.$$

$$2FeSO_4 + H_2SO_4 + (O) \rightarrow Fe_2(SO_4)_3 + H_2O.$$

$$H_2SO_3 + (O) \rightarrow H_2SO_4$$

$$4KMnO_4 + 4KOH \rightarrow 4K_2MnO_4 + 2H_2O + \overline{O_2}$$

$$2KMnO_4 + (heat) \rightarrow K_2MnO_4 + \overline{O_2}.$$

Experiment V.—Reactions of Manganous Salts.

Note.—Use a solution of manganous chloride, $MnCl_2$, in performing the following experiments.

(*a*) What color is imparted to the borax bead by manganese compounds when heated in the oxidizing flame? In the reducing flame?

(*b*) Mix a little manganous chloride with sodium carbonate and potassium nitrate, and fuse on a platinum foil. What is the color of the fused mass? Identify the substance (?).

(*c*) (1) To a dilute solution of manganous chloride add ammonium hydroxide. Result? Equation?

(2) Repeat (1) using a solution of manganous chloride to which has been added ammonium chloride. Result?

(*d*) Repeat (*c*) (1), using sodium hydroxide solution in excess. Equation? Treat the manganous hydroxide with bromine water.

(*e*) Repeat (*c*), using a solution of sodium carbonate or ammonium carbonate. Result? Prove that the precipitate is a carbonate (?). Equations?

(*f*) Add ammonium sulphide to a solution of manganous chloride. Prove that the precipitate is a sulphide (?). Equations?

(*g*) Pass hydrogen sulphide (generator in hood) through a solution of manganous chloride to which has been added 1 cm.^{3} of acetic acid. Account for the negative results.

(*h*) What is the color of the manganous ion? Of the manganate ion? Of the permanganate ion?

PROBLEMS.

1. A liter of a solution of potassium permanganate contains 10 grams of the salt. How many grams of ferrous sulphate, $FeSO_4$, can this solution oxidize to ferric sulphate, $Fe_2(SO_4)_3$, in the presence of the proper amount of sulphuric acid?

CHAPTER XXXIII.

TRANSITION ELEMENTS.

FIRST LONG PERIOD (IRON ELEMENTS).

Iron,	Fe.	55.9
Cobalt,	Co.	59.0
Nickel,	Ni.	58.7

The *iron elements* are among the most important elements technically, and are most interesting from the chemical stand-point.

These three elements, **iron, cobalt** and **nickel,** stand in a different relation to one another than the members of the other eight *groups*; i.e., they are not the corresponding members of successive *periods* as are the elements of the *families*. They belong to the *same period* and form a transition group between the first and second *series* of the first long *period*. (See Periodic Classification.) These three elements are closely related; in nature they are usually associated; the free metals are magnetic and possess many physical properties in common. They exhibit, however, a gradual transition in their chemical properties. Thus, iron forms *ferrates*, M'_2FeO_4, and two basic oxides, *ferrous* oxide, FeO, and *ferric* oxide, Fe_2O_3, each of which yields a series of stable salts of the type, $FeCl_2$ (ferrous chloride) and $FeCl_3$ (ferric chloride), respectively. Cobalt forms *cobaltous* and *cobaltic* salts, like $CoCl_2$ and $Co_2(SO_4)_3$. Many of the cobalt*ic* salts (except the double salts) are unstable. Nickel forms only one series of salts, namely, *nickelous* salts, like $NiCl_2$.

It is obvious that these metals are related, on the one hand, through iron, to chromium and manganese (recall such compounds as chromates, manganate and ferrates), and on the other hand, through nickel, to copper and zinc, both of which are bivalent elements and follow in the period.

IRON, Fe.

At. Wt. 55.9 Sp. Gr. 7.78.

Iron is one of the most abundant and widely distributed elements, yet it is found native in only small amounts in meteorites and certain volcanic ejects. Most of the rocks contain compounds of iron, and many of the red and yellow soils owe their color to the presence of iron compounds. Mineral waters holding iron compounds in solution are known as "*chalybeate waters*." Minute quantities of compounds of iron are also found in chlorophyl and in the hæmoglobin of the blood.*

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* Ammonium sulphide interacting with the iron compounds present in the tissues blackens the skin

The chief ores of iron are red *hematite* and *specular iron ore*, Fe_2O_3 (ores found in the Lake Superior region, particularly in northern Michigan, in Alabama, in Missouri and other regions of the United States); *limonite* or *brown* hematite, $2Fe_2O_3,3H_2O$ (ores found chiefly in Alabama and several other Southern States); *magnetite* or *magnetic iron ore* (loadstone), Fe_3O_4 (ores found in Pennsylvania, New York, Michigan and New Jersey); *franklinite*, similar to magnetite; and *siderite* or *spathic iron ore*, $FeCO_3$. Iron is also found in combination with sulphur as iron *pyrites* (Fool's gold), FeS. This pyrite is used in the manufacture of sulphuric acid. *Chalcopyrite*, a sulphide of iron and copper, contains small quantities of cobalt and nickel.

Iron ores are usually reduced by heating them with carbon and a flux in a *blast-furnace*. The nature of the flux depends on the composition of the iron ores; if the ores contain silica and clay, a flux of *basic* nature, like limestone, is used; and, conversely, ores mixed with lime or magnesia are heated with an *acid* flux, such as sand or clay-slate, in order that a fusible slag may be formed. An impure iron (pig iron) is obtained by this process.

(Discussions of the composition, properties and uses of *cast iron*, *wrought iron*, *spiegel iron* and *steel* will be found in the reference texts. The student is urged to become familiar with the principles involved in the manufacture of steel by such methods as the "Bessemer process," the "Thomas-Gilchrist process," and the "Siemens-Martin process" or "Open-hearth process.")

Pure iron may be prepared by reducing the oxide or oxalate in a stream of hydrogen; *electrolytic iron* may be deposited from solutions of certain salts by a properly regulated electric current; or the pure metal may be prepared by Goldschmidt's process.

It is a white, lustrous metal, ductile and more malleable than wrought iron. When finely divided it has a gray color. It is very tenacious; and it is to this property, together with its abundance and ease with which it can be prepared, that makes it the most valuable, industrially, of all metals. Pure iron melts at 1800°; wrought iron, at 1600°; and cast iron, 1100°–1300°. At red heat it becomes soft and can be welded. It is attracted to a magnet, but does not retain its magnetism. Iron is not acted upon by dry air at ordinary temperatures, but in moist air it becomes coated with a "*rust*" which is probably a mixture of the oxide and the hydroxide of iron, $2Fe_2O_3$, $(FeOH)_3$. It is not definitely understood just how the product* is formed. The alkali hydroxides or carbonates prevent rusting. At red heat, massive iron decomposes water, while finely divided iron decomposes water at 100°. Iron dissolves in dilute hydrochloric and sulphuric acids, hydrogen being evolved. Dilute nitric acid dissolves iron with the formation of ferrous nitrate and ammonium nitrate; concentrated nitric acid yields ferric nitrate and oxides of nitrogen. When steel and cast iron, which contain iron, iron carbide, Fe_3C, and graphite are treated with cold dilute acids almost pure hydrogen

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* The Corrosion of Iron, A. S. Cushman. Bul. No. 30, Dep't Agr.

is liberated, as the carbide and the graphite are not attacked; more concentrated acids, however, decompose the carbide, with the assistance of nascent hydrogen, the freed carbon combines with hydrogen forming hydrocarbons, which mix with the escaping gas, and give to it a very disagreeable odor. With nitric acid, the carbide carbon behaves in a slightly different manner. In this case the carbide passes into solution in combination with hydrogen and oxygen. This compound imparts a distinct color to the solution. Under similar conditions the depth of the color varies with the proportion of carbon present. The graphite, however, is set free and separates out as with other acids. When a piece of iron is immersed in very strong nitric acid (sp. gr. 1.42) for an instant and then removed, it is not attacked by ordinary nitric acid and is incapable of displacing hydrogen and other elements lying below it in the electromotive series. Iron exhibiting these peculiar properties is said to be in the *passive state.* Such iron loses these properties and becomes *active* when it is struck a sharp blow or is brought into contact with ordinary iron. It was formerly supposed that the apparent chemical inertness of the metal was due to the formation of a protecting layer of oxide over its surface, but it has been shown recently to the satisfaction of many that the passivity is due to an electrical condition of the metal.*

Nearly all of the compounds of iron are "*ous*" compounds in which the metal is a bivalent positive ion, or "*ic*" compounds in which iron is a trivalent positive ion. The oxides and hydroxides, FeO and $Fe(OH)_2$, Fe_2O_3 and $Fe(OH)_3$, are basic, the ferrous hydroxide being the stronger base. The ferric salts derived from $Fe(OH)_3$ are hydrolyzed to considerable extent. The ferrous salts are easily oxidized by the air to the ferric condition. Only a few *ferrates*, K_2FeO_4,$BaFeO_4$, are known. Such salts as potassium ferrocyanide, $K_4.Fe(CN)_6$ and potassium ferricyanide, $K_3.Fe(CN)_6$, yield complex anions which contain this element.

IRON, Fe.

At. Wt. 55.9 Sp. Gr. 7.8.

Experiment I.—Preparation of Iron by Reduction of Iron Oxide.

(*a*) Reduction by hydrogen. Assemble apparatus (Fig. 48) as described in Chapter IX, Experiment VIII. Observe the precautions suggested. Substitute iron oxide, Fe_2O_3, for the copper oxide in the porcelain boat. Are the particles of iron oxide attracted by the magnet? After the glass tube has been maintained at a red heat for 10 to 15 minutes, remove the heat and allow the boat and contents to cool in a stream of hydrogen. What was formed in the anterior portion of the tube? Examine the substance in the boat. What is its color? Are particles of it attracted by the magnet? Expose it to the air (?). Why did you cool the sub-

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* The Polarization Capacity of Iron and its Bearing on Passivity.—Jour. Amer. Chem. Soc., Nov., 1906.

stance in an atmosphere of hydrogen? Identify the substance (?). Equation? What is "Venetian red"?

(*b*) Goldschmidt's method (reduction with aluminum). Mix equal volumes of powdered iron oxide (hammer scale) and aluminum powder, and ignite (Caution!) the mixture on an iron plate or a brick. This latter operation is performed most readily by inserting a piece of magnesium ribbon in the mixture and setting fire to the projecting part. Result? Equation?

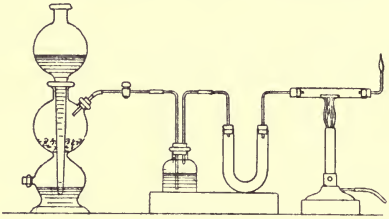

FIG. 48. (*Smith and Keller.*)

Note.—"Thermit" may be substituted for the above mixture.

Experiment II.—Properties of Iron.

(*a*) Examine cast iron, wrought iron and steel. Note their most obvious physical properties. Give the approximate composition of each. Examine a piece of piano wire; it is about 99.7 per cent. pure.

(*b*) Recall the behavior of a piece of iron heated to redness when plunged into a jar of oxygen. Equation? Recall or try the action of iron when treated with dilute acids. Equations?

Does iron "rust" in dry air? In moist air? Equation?

Experiment III.—Compounds of Iron.

(*a*) Examine the compounds of iron (end shelf). Give the color and *structural formula* of each compound. Record the valence of the iron atom in each compound, and state whether it manifests the properties of an acid-forming or base-forming element. Tabulate the above data.

(*b*) What is the formula, color and electrical charge of the ferrous ion, the ferric ion and the ferro-cyanide ion?

Hint.—Examine solutions of the salts which yield these ions (end shelf).

Experiment IV.—Preparation of Ferrous Sulphate.

Place about 20 grams of iron (free from rust) in the form of filings, nails or wire, in an Erlenmeyer flask in which there should be inserted a cork fitted with a glass jet to allow gas to escape. Pour on the iron 175 cm.^{3} of dilute sulphuric acid, add a few drops of concentrated acid and warm gently if the action appears slow. Note the odor of the escaping gases (?). Account for the odor. Allow the action to continue for 10 or 15 minutes, adding sufficient strong acid to keep up a brisk action, while other experiments are proceeded with. When nearly (but not quite) all of the iron has dissolved, filter into a casserole containing 2 cm.^{3} of sulphuric acid. Note the color of the solution and set it aside for a day. Pour off the mother liquid from the crystals, and wash the latter with cold water by decantation. Dry the crystals between sheets of filter paper. Note their color, taste, and solubility in water (?). Put a few of them into hard test tube and heat, gently at first, then strongly (?). Compare with the corresponding properties of ferrous sulphate, $FeSO_4 . 7H_2O$, crystals (end shelf). Identify the prepared crystals. Equation? Write the structural formula for ferrous sulphate. What is the valence of iron in this compound?

What is "green vitriol"? "oil of vitriol"? "copperas"? "white viriol"? iron protosulphate? writing ink (black)?

Experiment V.—Preparation of Ferrous Ammonium Sulphate (Mohr's Salt).

Weigh 5 grams of ferrous sulphate into an evaporating dish or a casserole; calculate the weight of and weigh out an equi-molecular quantity of ammonium sulphate. Dissolve the salts separately in the smallest volume of hot water. Add a few drops of sulphuric acid to the solution of ferrous sulphate. Mix the solutions. Allow the mixture to cool slowly and evaporate spontaneously (?). Describe the crystals and compare them with those in the laboratory (end shelf). Collect the crystals in a funnel, the stem of which is closed with a loose plug of glass-wool (or better, provided with a platinum filter cone), allow the mother liquid to drain off, then wash the crystals with a small quantity of cold water and dry with filter paper.

Is "Mohr's Salt," $(NH_4)_2SO_4,FeSO_4,6H_2O$, a complex or compound salt? Reason for your answer? Equation?

Experiment VI.—Preparation of Ferric Ammonium Sulphate, Iron-Ammonium Alum.

Directions are the same as those given in Experiment VI, except that ferric sulphate, $Fe_2(SO_4)_3$, is used instead of ferrous sulphate. Equation?

To which class of salts, complex or compound, does iron-ammonium alum, $(NH_4)_2SO_4,Fe_2(SO_4)_3,24H_2O$, belong?

Experiment VII.—Hydrolysis of Ferric Salts.

Dissolve equal weights (about 0.5 gram) of ferrous sulphate (use ferrous ammonium sulphate) and ferric sulphate, $Fe_2(SO_4)_3$, in equal volumes of water in separate test tubes, then warm slightly. Observe the color of each by looking down through the solution at a piece of white paper (?). Test each solution with litmus paper (?). Add 2 or 3 cm.^{3} of pure concentrated sulphuric acid to each solution and observe the colors again (?). What is the color of the ferrous ion? The ferric ion is almost colorless?* Ferric hydroxide, $Fe(OH)_3$, is a reddishb-rown substance. Can you account for the change in color of the solution of the ferric salt? Ionic equations? Which manifests the stronger basic properties—iron in the "ous" or iron in the "ic" condition?

Experiment VIII.—Reactions of Ferrous and Ferric Salts.

(*a*) Make a borax bead and dissolve in it a small quantity of any iron compound (preferably, the oxide); treat the bead successively with the oxidizing (?) and reducing flames (?). Use a recently prepared solution of ferrous sulphate (ferrous ammonium sulphate) and a dilute solution of ferric chloride, $FeCl_3$, for the following reactions. Treat a portion of each, separately, with the following reagents. Compare the two results obtained with each reagent.

(*b*) Ammonium hydroxide (?). Equations? Allow the tubes and their contents to stand exposed to the air for 15 or 20 minutes. Result? Equations?

(*c*) Sodium hydroxide solution (?). Equation? Do the precipitates dissolve in excess of the precipitant?

(*d*) Sodium carbonate (?). Prove by proper tests that the precipitates do or do not contain the carbonic acid radical. Equations?

(*e*) A few drops of a solution of potassium ferricyanide, $K_3Fe(CN)_5$ (?). Equation? What is "Turnbull's blue?"

(*f*) A few drops of a potassium ferrocyanide, $K_4Fe(CN)_3$, solution (?). Equation? What is "Berlin or Prussian blue?"

(*g*) Several drops of a potassium thiocyanate, KCNS, solution? Equation? Inasmuch as the ferric ion and the thiocyanate ion are *colorless*, what is probably the source of the color?

(*h*) What reagents would you use to test for the presence of the ferrous ion? For the ferric ion?

Note.—Potassium ferrocyanide, potassium ferricyanide and potassium thiocyanate belong to a class of substances known as "*indicators*."† By their use we are enabled to detect, for example, the presence of the iron ion, and to determine also its state of oxidation; i.e., whether it is in the "ous" or "ic" condition. The use of potassium thiocyanate constitutes a very delicate test for detecting traces of the ferric ion.

Experiment IX.—Ferrocyanides and Ferricyanides.

Using diluted solutions of potassium ferrocyanide, apply tests as given in Experiment VIII, (*b*), (*c*), (*d*), to ascertain whether either the ferrous

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* The ferric ion is almost colorless. The yellowish-brown color of solutions of ferric salts is due to the presence of ferric hydroxide (reddish-brown) produced by hydrolysis.

† See Ostwald's Scientific Foundations of Analytical Chemistry.

or ferric ions are present or not. Result? Is potassium ferrocyanide a "complex" or a "compound" salt? Why? Indicate by an equation how it probably dissociates. (See note, Chapter XXV. Experiment XVII.)

Experiment X.—Reactions of Iron Salts Involving Oxidations and Reductions.

(*a*) Action of hydrogen sulphide on iron salts.

1. Saturate a dilute solution of a ferrous salt (ferrous-ammonium sulphate) with hydrogen sulphide (?). Add ammonium hydroxide (?). Filter, wash thoroughly the precipitate with cold water, and ascertain whether it is a sulphide or hydroxide. Explain in terms of the *ion-product constant* why hydrogen sulphide does not not precipitate all of the iron from solutions of its ferrous salts. Ferric salts are reduced by hydrogen sulphide.

2. Pass hydrogen sulphide into a dilute solution of ferric chloride (?). Filter. Test the precipitate by burning it on a piece of filter paper (note the odor) (?). Test the filtrate for the presence of ferrous ions (?).

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + \underline{S.}$$
$$2Fe''' + S'' \longrightarrow 2Fe'' + \underline{S.}$$

(*b*) Action of ammonium sulphide.

1. Ammonium sulphide precipitates black ferrous sulphide, FeS, from solutions of ferrous salts.

2. Ferric salts are reduced by ammonium sulphide. The latter produces a black precipitate of ferrous sulphide, soluble in hydrochloric acid.

$$2FeCl_3 + 3(NH_4)_2S \longrightarrow \underline{2FeS} + 6NH_4Cl + S.$$

(*c*) Reduction of ferric salts to ferrous salts.

1. By nascent hydrogen. Place a few pieces of granulated zinc in a small flask which is fitted with a cork provided with a glass jet for the escape of gases. Pour 20 cm.³ of ferric chloride into the flask and add an equal volume of water. Now add sufficient hydrochloric acid to dissolve the zinc with a rapid evolution of hydrogen. The action is hastened by warming gently. Test a portion of the solution for the presence of ferrous ions (?). Is the ferric ion present (test)? Equations?

2. By stannous chloride. To 3 cm.³ of a solution of ferric chloride in a test tube add 1 cm.³ of stannous chloride. Test portions of the solution as in (*a*), 1. Equations?

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$
$$2Fe''' + Sn'' \longrightarrow 2Fe'' + Sn''''$$

(*d*) Oxidation of ferrous salts to ferric salts.

1. By nitric acid. Into 5 cm.³ of a hot dilute solution of ferrous

sulphate, to which a little sulphuric acid has been added, pour 5 cm.³ of concentrated nitric acid drop by drop. Test separate portions of the liquid for the presence of ferrous and ferric ions (?). Make a record of all tests and results. Equations?

$$2HNO_3 \rightarrow (3O) + 2\overline{NO} + H_2O.$$
$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2\overline{NO}.$$
$$6FeCl_2 + 3HCl + 2HNO_3 \rightarrow 6FeCl_3 + 4H_2O + 2\overline{NO}.$$

2. By potassium bichromate in the presence of an acid. Pour 5 cm.³ of dilute sulphuric acid into 15 cm.³ of ferrous sulphate solution in a small beaker. Now add by means of a burette a solution of potassium bichromate drop by drop until a drop of the solution of iron salt transferred to white porcelain and tested with potassium ferricyanide solution fails to give a blue color. This test shows the absence of what ion? Test drops of the solution with a solution of potassium ferrocyanide or a solution of potassium thiocyanate. Result? This test is made to detect the presence of which ion? Equations?

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + (3O).$$
$$6FeSO_4 + 3H_2SO_4 + (3O) \rightarrow 3Fe_2(SO_4)_3 + 3H_2O.$$

3. By potassium permanganate in the presence of an acid. Measure accurately 15 cm.³ of a recently prepared solution of ferrous sulphate (ferrous-ammonium sulphate) into a small clean beaker, and add 5 cm.³ of dilute sulphuric acid. Clamp a clean burette into a vertical position and fill it with a solution of potassium permanganate (end shelf). Allow this latter solution to drop slowly into the ferrous salt. The pink color of the permanganate immediately disappears on stirring with a glass rod (do not remove the rod from the solution). The color continues to be destroyed until all of the ferrous salt is completely *oxidized* to the ferric state, when a drop of permanganate added in excess imparts a faint pink color to the liquid. This *indicates* the *end point*; i.e., that the reaction is ended. Record the number of cm.³ of potassium permanganate required to oxidize the ferrous salt.

By applying suitable tests to portions of this liquid, prove that the oxidation has been complete; i.e., that the ferrous ion is not present and that ferric ions are present. Make a record of tests employed and results secured.

Repeat the experiment, using 20 cm.³ of ferrous sulphate solution. Equations?

4. Chlorine water, bromine water, and potassium chlorate in the presence of strong hydrochloric acid, are other oxidizing agents frequently used to convert ferrous into ferric salts.

5. Add 5 cm.³ of pure concentrated nitric acid to 50 cm.³ of tap-water; evaporate to 15–20 cm.³ and test for the presence of the ferric ion (?).

COBALT, CO.

At. Wt. 59.0 Sp. Gr. 8.5.

The principal ores of **cobalt** are *smaltite*, $CoAs_2$, and *cobaltite*, CoAsS. The pure metal may be obtained by reducing the oxide, the chloride or the oxalate in a stream of hydrogen or by Goldschmidt's process. Cobalt resembles iron in many respects. It is a lustrous silver-white (pink-tinted), hard metal, malleable, tenacious, and when heiated is very ductile. It melts at about 1500°. Unlike iron and nickel,t retains its magnetic properties even at red heat. The metal has but few commercial applications, its use being confined to the iron and steel industry.

Cobalt in the massive form is not readily acted upon by the air, but the finely divided metal, especially when it is freshly prepared by the reduction of the oxide in hydrogen, oxidizes easily and may take fire spontaneously in the air. It is attacked slowly by dilute acids, hydrogen being liberated.

Cobalt, like iron, forms two kinds of ions—the cobaltous ion, Co'', and the cobaltic ion, Co'''. The *cobaltous salts* are but slightly hydrolyzed, but the *cobaltic salts* are completely decomposed by water. The latter are rather unstable and tend to break down into the cobaltous salts with a liberation of one-third of the acid radical. Most of the cobaltous compounds are red when hydrated and blue when dehydrated. The blue color of the salt is explained by some chemists as being due to the "repression of the ionization of the salt"; i.e., "to the driving back of the ions into molecules, which are blue." Cobalt shows a marked tendency to enter into combination with the ions, NO_2, CN and NH_2, to form derivatives which yield many complex ions which usually give none of the reactions of cobalt ions. The cobalt compounds give with ammonia many complex compounds which present some very complex relations. One of the most interesting series of these complex salts is known as the *cobalt amines*.

Some of the more important compounds are represented by the following formulæ:

Cobaltous compounds, CoO, $Co(OH)_2$, $CoCl_2$, $6H_2O$, $CoSO_4,6H_2O$, $Co(NO_3)_2.6H_2O$, $CoCO_3.6H_2O$, CoS, $Co_2(Fe(CN)_6)$, $Co_3(Fe(CN)_6)$, $Co(CN)_2$, $K_4Co(CN)_6$; cobaltic compounds, Co_2O_3, $Co(OH)_3$, $Co_2(SO_4)_3.18H_2O$, $K_3Co(NO_2)_6$; cobalt amines, $Co(NH_3)_3Cl_3.H_2O$, $Co(NH_3)_4Cl_3.H_2O$, $Co(NH_3)4Cl_3.H_2O$, $Co(NH_3)_5Cl_3$, etc.

Experiment I.—Properties of Cobalt.

Examine cobalt metal and note its most obvious physical properties (?). Scratch the metal with the point of a knife blade. Is the metal hard? Does it tarnish readily in the air?

Experiment II.—Cobalt Compounds.

Examine the compounds of cobalt (end shelf). Give the color and empirical formula of each compound. Record the valency of the cobalt atom in each compound. What is the color of the cobalt ion?

Experiment III.—Dehydration of Hydrated Cobaltous Chloride.

Write upon a sheet of your note-book with a solution of cobalt chloride by means of a glass rod. Allow it to dry, then warm the paper very gently by holding it at some distance from a gas flame. Result? Breathe upon the paper or hold it for an instant in a current of steam. Explain the changes in color. Equations? What is "sympathetic ink"?

Experiment IV.—Reactions of Cobalt Salts.

Treat separate portions of a solution of cobalt chloride with the following reagents:

(*a*) Test the solution with a borax bead in the oxidizing (?) and reducing (?) flames.

(*b*) Ammonium hydroxide, first in small quantities (?), then in excess (?). Equations?

(*c*) Sodium hydroxide solution, first in small quantities (?), then in excess (?). Add bromine water and boil (?). Equations?

(*d*) Ammonium sulphide solution (?). Filter. Try the effect of dilute hydrochloric acid upon the precipitate (?). Equations?

(*e*) Potassium cyanide solution, first in small quantities (?), then in excess (?); add sodium hydroxide solution in considerable quantity, then bromine water* until the color of bromine persists; warm gently. Results (?) Equations?

NICKEL, Ni.

At. Wt. 58.7 Sp. Gr. 8.8–9.0

This element possesses many properties in common with cobalt. It occurs chiefly in combination with arsenic as *niccolite*, NiAs, and *nickel glance*, NiAsS. It is now manufactured chiefly from *garnierite*, $H_4Ni_2Mg_2(SiO_4)_3.4H_2O$, a silicate found in Australia. The crude nickel may be obtained from granierite by reducing the ore in a blast furnace or by electrolysis. Pure nickel is usually prepared by reducing the oxide with carbon at a high temperature or by reducing the oxide in a stream of hydrogen.

Nickel is a lustrous, white metal (yellow-tinted), very hard and tenacious, with a melting point at 1570°. It takes a very high polish. It tarnishes very slowly, even in moist air. On account of its resistance to oxidation, it is used extensively as a protective covering for other metals which are more readily oxidized, such as iron, etc. The process of depositing one metal upon another by electrolysis is known as *electroplating*. Nickel forms a number of valuable *alloys*. *German* silver is an alloy of copper, nickel and zinc (2 to 1 to 1). Our co-called "nickel" of

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* Bromine is much more solublein an aqueous solution of potassium bromide than in water.

currency contains 75 per cent. copper and 25 per cent. nickel. *Nickel-steel* contains from 4 to 15 per cent. of nickel.

Hydrochloric acid and sulphuric acid attack nickel with difficulty, but nitric acid acts upon it very readily. Concentrated nitric acid renders the metal "passive."

Nickel forms a bivalent ion, *nickelion*, Ni'', which is of green color. Nickel can form a higher stage of oxidation, for example, Ni_2O_3 and $Ni(OH)_3$, but they are extremely unstable and do not behave as base-forming compounds.

Nickel can also form complex ions, but these are neither so numerous nor so stable as those of cobalt; this forms the essential difference between the chemical conduct of these two elements. The complex ions of nickel containing ammonia also differ from those of cobalt not only in being derived from bivalent nickel, but also in being very unstable.

Most of the nickel salts are green when hydrated and yellow when dehydrated.

The following formulæ show the composition of some of the more important compounds of nickel: Nickelous compounds, NiO, $Ni(OH)_2$, $NiCl_2.6H_2O$, $NiSO_4.6H_2O$, $Ni(NO_3)_2.6H_2O$, $NiCO_3.6H_2O$, NiS, $Ni_2(Fe(CN)_6)$, $Ni_3(Fe(Cn)_6)_2$, $Ni(CN)_2$, $Ni(CN)_2$, $2KCN$; nickelic compounds, Ni_2O_3, $Ni(OH)_3$.

Experiment I.—Properties of Nickel.

Same as Experiment I, "Cobalt."

Experiment II.—Nickel Compounds.

Same as Experiment II, "Cobalt."

Experiment III.—Reactions of Nickel Salts.

Same as Experiment IV, "Cobalt." A solution contains both the nickel and cobalt ions. How may the cobalt be separated from the nickel?

PROBLEMS.

1. It was found that 1.586 grams of iron formed 2.265 grams of ferric oxide. Calculate the atomic weight of iron.
2. How many grams of potassium bichromate will be required to oxidize 10 grams of ferrous sulphate?
3. How many grams of potassium permanganate will be required to oxidize 10 grams of ferrous sulphate?
4. What weight of stannous chloride will be required, theoretically, to reduce 1 gram of ferric chloride to ferrous chloride?

CHAPTER XXXIV.

TRANSITION ELEMENTS

Second Long Period.	Fourth Long Period.
(Ruthenium, Ru. 101.7)	(Osmium, Os. 191.0)
(Rhodium, Rh. 103.0)	(Iridium, Ir. 193.0)
(Palladium, Pd. 106.5)	Platinum, Pt. 194.8

These rare metals constitute two separate transitional groups, yet they are very closely related to one another. Again, they possess certain properties which are markedly different. The first three have atomic weights which are close to one hundred, while the atomic weights of the last three are close to two hundred. The specific gravities show a similar relation, as may be seen from the following table:

I.	Ru, sp. gr.	12.26;	Rh, sp. gr.	12.10;	Pd, sp. gr.	11.9;
II.	Os, sp. gr.	22.38;	Ir, sp. gr.	22.4;	Pt, sp. gr.	21.45.

All of these elements, however, resemble **platinum** more or less closely. They are therefore spoken of as the *platinum elements*. In nature they occur associated together in what is commonly known as *platinum ore*. This ore, which is sometimes spoken of as *native platinum*, is found in small particles and nuggets in river sand and alluvial deposits. The Urals furnish the larger portion of the world's supply; smaller quantities are found in Australia, California, Borneo and Brazil. The ore contains these elements in the metallic state, more or less alloyed, together with small quantities of iron, copper and gold. Platinum constitutes 60 to 85 per cent. of the ore. Smaller amounts of platinum are found alloyed with iridium.

The members of these groups are lustrous, white metals, unacted upon by air at ordinary temperatures. Osmium burns in oxygen when highly heated, forming the tetroxide, OsO_4. The other five metals resist oxidation at any temperature.

Palladium is the only member which is attacked by nitric acid. The other members are not acted upon by ordinary acids. *Aqua regia* is without action upon rhodium and iridium.

Rhuthenium is a hard, brittle metal, fusing at about 2000°. It was discovered by Claus in 1845. Some of its compounds are RuO, Ru_2O_3, RuO_2, RuO_4, $Ru(OH)_3$, $Ru(OH)_4.3H_2O$, $RuCl_2$, $RuCl_3$, $RuCl_4$, K_2RuO_4, $KRoO_4$.

Rhodium is a malleable metal, fusing at 2000°. In appearance, it resembles aluminum. It is harder than platinum. It was discovered by

Wollaston in 1803. Some of its compounds are, RhO, Rh_2O_3, RhO_2, $Rh(OH)_3$, $Rh(OH)_4$, $RhCl_3$.

Palladium is the most easily fusible of these metals, melting at about 1500°. It possesses the property of absorbing (occluding) large volumes of hydrogen gas, 360 to 960 times its own volume, depending upon its state of aggregation and its temperature. When heated to 130°, it surrenders the hydrogen. It has been supposed for a long time that the hydrogen and palladium enter into a definite chemical union with the formation of palladium hydride, Pd_2H. There is considerable doubt as to whether this is a definite chemical compound. The later explanation that palladium-hydrogen is simply a "solid solution" in which hydrogen is dissolved in palladium does not satisfactorily account for all of the observed phenomena. Palladium-hydrogen is a powerful reducing agent owing to its capability of releasing hyrogen in a condition similar to "nascent" hydrogen Some of its compounds are Pd_2O, PdO, $PdCl_2$, $PdCl_4$, PdI_2, $Pd(NO_3)_2$, $PdSO_4.2H_2O$, H_2PdCl_6, K_2PdCl_6, $(NH_4)_2PdCl_6$.

Osmium is the heaviest known elementary substance. It fuses at 2500°. An alloy of iridium and osmium which is very hard is used for tipping gold pens. A solution of osmium tetroxide, OsO_4, is found useful in hardening tissues for histological purposes. Some of its more important compounds are represented by the following formulæ: OsO, Os_2O_3, OsO_2, OsO_4, $Os(OH)_2$, $Os(OH)_3$, $OsCl_2$, $OsCl_3$, $OsCl_4$, K_2OsO_4.

Iridium is a very hard metal fusing at 1950°. It alloys with platinum and enhances the resistance of that metal to the action of acids. It is, therefore, usually present in platinum utensils designed for laboratory purposes. The following formulæ represent some of its compounds: IrO, Ir_2O_3, IrO_2, $Ir(OH)_4$, $IrCl_2$, $IrCl_3$, $IrCl_4$, $K_3IrCl_6.3H_2O$.

Platinum is a tough, malleable, ductile metal which can be welded at red heat It fuses at 1770°. Its temperature coefficient of expansion is about the same as that of glass. Therefore, if it is desired to seal an electrical connection through glass, a platinum wire which is a good conductor is the most convenient means. This fact is utilized in constructing incandescent electric lights.

Platinum occludes oxygen and hydrogen, the quantity absorbed depending upon the state of division of the metal. *Platinum black* (very finely divided platinum) which can be prepared by depositiong it from its solutions by means of a more electro-positive metal, absorbs* about 300 times its own volume of hydrogen and about 100 times its own volume of oxygen. At red heat the gases are expelled from the metal. The value of platinum as a "catalytic agent" is due to its capacity to occlude gases.

Platinum is very resistant to chemical reagents, and upon this fact its value largely depends. It is not attacked by the ordinary acids, but the free chlorine in *aqua regia* converts it into chloroplatinic acid, H_2PtCl_6. It is not acted upon by the fused alkaline carbonates, but it interacts with the fused alkalies, giving platinates. The fused alkaline cyanides also

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* Hydrogen is "dissolved," but oxygen is merely concentrated upon its surface.

interact with it. Platinum must not be heated in contact with carbon, silicon and phosphorus, as they unite with it forming compounds which are quite brittle. Lead and antimony form fusible alloys with platinum, therefore neither these metals, nor compounds from which they may be liberated, should be heated in platinum vessels.

Platinum forms compounds in which it is the positive ion showing a valence of II or IV, as well as compounds in which it is a constitutent of the negative ion. However, when solutions containing ions, in which platinum is in the anion, are electrolyzed, the platinum is deposited at the anode and not at the cathode. The following list contains some of the more important compounds of platinum: *Platinous compounds*, PtO, $Pt(OH)_2$, $PtCl_2$, PtS; *Platinic compounds*, $Pt(OH)_4$, $PtCl_4$, PtS_2; *chloroplatinic acid*, H_2PtCl_6; *chloroplatinates*, K_2PtCl_6, Na_2PtCl_6, $(NH_4)_2PtCl_6$; *platinocyanides*, $BaPt(CN)_4.4H_2O$, $K_2Pt(CN)_4,3H_2O$.

Experiment I.—Properties of Platinum.

(*a*) Physical properties. Examine specimens of platinum foil and wire. Note the physical properties of the metal (?). Hold a piece of platinum wire in the hottest portions of the Bunsen flame (?), and the flame of the blast-lamp (?). What is "spongy platinum"? "Platinum black"?

(*b*) Chemical properties. Does platinum tarnish readily when exposed to the action of the air. Procure two small pieces of platinum scrap from the assistant. Place them in separate test tubes. Heat the one with hydrochloric acid (?) and the other with nitric acid (?). Mix the contents of both test tubes. Result? Equation?

Experiment II.—Platinum as a "Catalytic Agent."

Recall or repeat those experiments in which platinum acted as a "catalytic agent." State briefly Ostwald's tentative explanation of the rôle of a catalyzer. (See Chapter IX, Experiment VII.)

Experiment III.—Platinum Compounds.

Examine the compounds of platinum (end shelf). Give the color and formula of each compound. What is the color of the platinum ion?

Experiment IV.—Preparation of Platinic Chloride.

(*a*) Scour pieces of platinum scrap with sea sand, then wash with distilled water, and boil with hydrochloric acid. Decant the liquid, and again wash with distilled water. Dissolve 1 gram of the platinum in 25 cm.^{3} of *aqua regia* in a covered glass dish. After the "spurting" has ceased pour off the supernatant fluid and concentrate it in a glass dish by evaporation on the steam bath. In the meantime add more *aqua regia* to the undissolved platinum, and continue the above operations until all of the platinum is dissolved. After the combined solutions have been evaporated to dryness, moisten with a little hydrochloric acid and take up with water, or, (*b*) The platinum may be precipitated from the concentrated *aqua-regia* solution by a strong ammonium chloride solution, as ammonium chloroplatinate, $(NH_4)_2PtCl_6$. Filter, ignite the precipitate in a porcelain crucible. Boil the residue of "spongy platinum" with hydrochloric acid, decant the liquid and dissolve the platinum in *aqua regia*. Evaporate the solution to dryness on the steam bath, moisten the residue with hydrochloric acid and again evaporate just to dryness. Take up the product with distilled water. Equations?

Experiment V.—Reactions of Platinum Salts.

(*a*) Dilute a small quantity of a platinic chloride solution with 2 or 3 $cm.^3$ of water, add a solution of hydrogen sulphide, and warm slightly (?). Is the precipitate soluble in excess of potassium hydroxide? In ammonium polysulphide?

(*b*) Reduction of platinum salts. "Platinum black".* To a solution of platinic chloride add an excess of sodium carbonate solution and a little grape sugar, then boil the mixture. Carbon dioxide is evolved, and a black powder ("platinum black") is formed slowly. The solutions should be dilute. Wash the powder successively with dilute alcohol, hydrochloric acid, potassium hydroxide solution, distilled water, and then dry it by applying a gentle heat.

(*c*) Recall the interactions of solutions of platinic chloride with the alkaline chlorides. (See "Sodium," "Potassium," and "Ammonium.")

For a discussion of the properties of **praseodymium, neodymium, samarium, gadolinium, terbium, erbium, thulium, ytterbium,** etc., see reference texts.

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* "Platinum black" is a more effective catalyzer than "spongy platinum."

CHAPTER XXXV.

RELATIONS WITHIN THE GROUPS OF THE PERIODIC CLASSIFICATION.

TABLE.

Grouping of the Metals (Cations) for Purposes of Analysis.

METALS (CATIONS)

I. Metals which are precipitated from solutions by HCl

Silver
Mercury (ous)
Lead

Metals which are not precipitated from solutions by HCl

II. Metals which are precipitated from solutions containing hydrochloric acid by H_2S

Div. A. Mercury (ic)
Copper
Cadmium
Bismuth

Div. B. Arsenic
Antimony
Tin
Gold
Platinum
} Sulphides soluble in ammonium polysulphide.

Metals which are not precipitated from solutions containing hydrochloric acid by H_2S

III. Metals precipitated from ammoniacal solutions containing ammonium chloride by $(NH_4)_2S$

Cobalt
Nickel
Iron Chromium
Aluminum
Zinc
Manganese

Metals not precipitated from ammoniacal solutions containing ammonium chloride by $(NH_4)_2S$

IV. Metals which are precipitated from solutions by $(NH_4)_2CO_3$

Barium
Calcium
Strontium

Metals which are not precipitated from solutions by $(NH_4)_2CO_3$

V. Metal which is precipitated from solutions by $NaNH_4HPO_4$

Magnesium

VI. Metals which are not precipitated from solutions by $NaNH_4HPO_4$

Detected by special tests { Sodium
Potassium
Ammonium

TABLE.

Grouping of Non-metallic Radicals (Anions) for Purposes of Analysis.

Acid-radicals (Anions)

I. Radicals which are precipitated from neutral solutions by $BaCl_2$	Radicals which are not precipitated from neutral solutions by $BaCl_2$

Sulphuric, H_3SO_4 Hydrofluosilic, H_2SiF_6	Barium salts insoluble in dilute hydrochloric acid.
Boric, H_3BO_3 Carbonic, H_2CO_3 Citric, $H_3(C_6H_5O_7)$ Chromic, H_2CrO_4 Hydrofluoric, HF Iodic, HIO_3 Oxalic, $H_2(C_2O_4)$ Phosphoric, H_3PO_4 Sulphurous, H_2SO_3 Silicic, H_2SiO_3 Tartaric, $H_2(C_4H_4O_6)$ Thiosulphuric, $H_2S_2O_3$	Barium salts soluble in dilute hydrochloric acid.

II. Radicals precipitated from solutions acidified with nitric acid by $AgNO_3$	Radicals which are not precipitated from solutions acidified with nitric acid by $AgNO_3$
Ferricyanic, $H_3Fe(CN)_6$	Acetic, $H(C_2H_3O_2)$
Ferrocyanic, $H_4Fe(CN)_6$	Chloric, $HClO_3$
Hydrochloric, HCl	Perchloric, $HClO_4$
Hydrobromic, HBr	Cyanic, HCNO
Hydriodic, HI	Formic, $H(CHO_2)$
Hydrocyanic, HCN	Nitric, HNO_3
Hydrosulphuric, H_2S	Nitrous, HNO_2
Thiocyanic, HCNS	

APPENDIX I.

PRELIMINARY EXERCISES.

APPARATUS.

Since chemistry is pre-eminently an experimental science, it is in order to begin work by examining various pieces of apparatus and acquainting one's self with their manipulation.

THE BUNSEN BURNER.

Carefully examine the Bunsen burner (Fig. 49). Take it apart; assemble it, noting relation of parts. Connect it with the gas supply. Light the burner by turning on the gas, and then holding a lighted match near the side of the burner a short distance below the top. Notice the effect of opening and closing the holes at the bottom of the tube. Explain. Adjust the opening until the luminous region has just disappeared and the flame is noiseless: this is the "Bunsen flame." A flame 6 cm. to 9 cm. high is adapted to most work. If soot is deposited upon the object being heated, open the holes at the foot at the tube, but not so far as to produce a noisy flame.

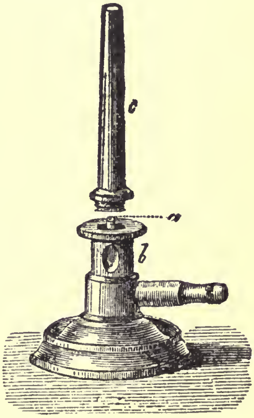

FIG. 49.—Bunsen Burner.

Now study the structure of the flame. Determine which parts are relatively hotter and which cooler. Introduce *quickly* into the center of the flame (the darker portion), about one-half of a centimeter above the burner, the head of a match. Results? Can you insert a match as per above directions and withdraw it without igniting same?

Hold a piece of platinum wire across the flame in various places. Note the color of the wire. Bring quickly and horizontally (to desk top) a piece of heavy pasteboard into the flame, about 2 cm. above the top of the tube; hold it quietly for several seconds, then remove quickly. Do you find a brown (scorched) circle? Explain.

To secure the greatest heating effect, place object just above apex of the dark inner cone of unburned gas. Why is there a cone of unburned gas? Why the shape? If oxygen is necessary for the combustion of the gas, where might the gas escape for a time unburned?

Half fill a test tube with water. Be sure that the outside of the tube is dry. By means of test tube holders, introduce the tube into the hottest region of the flame, inclining the tube at an angle of about 45° to the top of the desk. Heat only that portion of the tube containing the liquid: if the flame strikes the tube above the liquid, the tube may crack. Keep the liquid in the tube slightly agitated by a short, quick movement of the hand.

Above directions should be observed in all cases where liquids are heated in test tubes. A "wing-top" attachment gives a broad flame of very much use to the glass-blower.

Note.—If gas is not available in the laboratory and alcohol lamps are used, perform as many as possible of above experiments.

THE BLAST-LAMP.

Where a much higher temperature is required than can be secured by means of the Bunsen burner, the blast-lamp is used. The size of the flame can be altered by proper manipulation. (Instructions from assistant.)

MANIPULATION OF GLASS.

I.—To Cut Glass Tubing.

(*a*) Lay the tubing on a flat surface; make a file-mark on it at right angles to the length; take the tube in the hands, placing the two thumbs opposite the scratch and the fingers on either side of the scratch; now push gently with the thumbs and at the same time pull the hands apart, the tubing usually breaks squarely at the scratch. "Fire-polish" the ends of tube by turning them slowly in the Bunsen flame.

(*b*) To break large tubing or cut off bottoms of bottles, etc., encircle tube with wire or make an ink-mark to trace the path of the desired break or cut, then a file-mark is made upon the surface on mark; a steel file handle, or better, a glass rod heated in the blast-lamp flame until it is red hot, when it is at once pressed against the scratch until the glass begins to crack. The fracture can usually be led in any direction by keeping the hot glass rod in front of it. Heat rod frequently to keep it red hot.

II.—Grinding Glass.

(*a*) Rough edges of tubes or bottles may be ground down to bell-jar effect by spreading emery paste upon a smooth flat surface and rubbing broken edges upon it.

(*b*) Glass stoppers may be ground into necks of flasks, etc., by covering stoppers and inside of neck with emery paste, and then imparting a gentle pressure to stopper while twisting it into place.

III.—Cutting and Perforation Glass Plates.

(*a*) The plate of glass is laid upon a flat surface; "glass cutters" are used to make the scratch where the break is desired. "Glass cutters" are usually made with a rotating wheel of steel or a diamond point.

(*b*) Holes can be made in a glass plate by the aid of a broken end of a round file kept wet with a solution of camphor in oil of turpentine.

IV.—To make Stirring Rods.

Cut off a piece of glass tubing 18 cm. to 20 cm. long and 6 mm. in diameter. Hold the ends of the tube successively in a Bunsen flame, rotating the tube constantly until the open ends are sealed. Glass rods may be used instead.

V.—To Bend Glass Tubing.

A flat Bunsen flame, produced by a "wing-top" or a "fish-tail" attachment, is used for bending glass. Take the tube in both hands and hold that portion which is to be bent lengthwise to the flame and just above the flame until it is warmed; then place it in the flame, constantly rotating on the long axis, between thumb and fingers, until glass becomes fairly soft; remove it from flame and quickly bend it into the desired form. It is well to anneal the glass at the bend by "smoking" it. This may be accomplished by closing the holes at the base of the burner, thus producing a smoky flame. The bent portion should not be permitted to touch cold objects until it has cooled.

Using ordinary glass tubing, the student should make various styles of bends like models shown by the assistant. Always "fire-polish" the edges of glass tubing.

Note.—To increase the internal diameter of tubes for insertion of corks, etc., soften the tube in the flame, and insert a conical piece of charcoal by gentle pressure until tube spreads into desired shape.

VI.—Joining Tubes and Glass Blowing.

See Ostwald's "Physico-Chemical Measurements," pages 66–72, also Shenstone's "Methods of Glass Blowing." The student will find in said references brief but excellent discussions of the subject.

VII.—Sealing Platinum Wires into Glass Tubes.

Soften a glass tube; draw it out; cut off short, and by heating cause the end to fall nearly together, or until the wire can just be pushed into the opening; heat until glass closes around the wire.

More certain results are obtained if the platinum wire receives a drop of melted enamel (tough lead-glass) at the proper place and is pushed through opening in tube until hole is closed by the enamel. The enamel unites well with platinum and also with ordinary glass.

PERFORATION OF STOPPERS.

A set of cork borers may be secured from the assistant. (T.O.) Hold the cork in the hand and bore from the *narrow* end. Avoid great pressure on the cork borer.

In perforating rubber corks, the borer cuts more easily if it is dipped frequently into a solution of caustic soda. A round file may be used to smooth the perforation.

TREATMENT OF RUBBER CORKS AND TUBING.

Where rubber is to be used in quantitative experiments, it should be boiled in dilute sodium hydroxide solution, rinsed with water, then boiled in dilute hydrochloric acid, and finally washed with water. This operation removes impurities which frequently introduce errors.

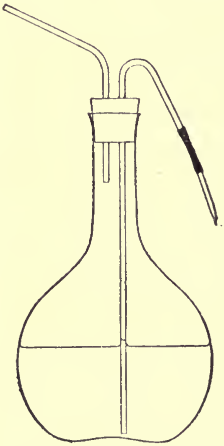

Fig. 50.—Water Bottle.

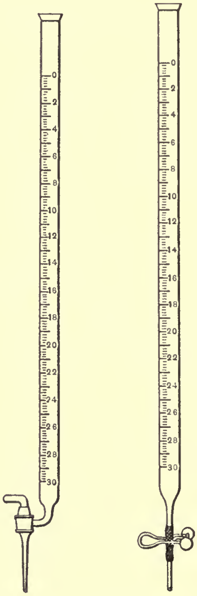

Fig. 51.—Mohr Burettes.

CONSTRUCTION OF PARTS AND THE ASSEMBLING OF A WASH BOTTLE.

Select proper material and construct a wash bottle (Fig. 50) like model in laboratory. The necessary material will be found in the drawer.

MEASURING INSTRUMENTS.

(*a*) Measures of volume.

Assemble the Mohr (Fig. 51); or Geissler burette, and clamp it in a vertical position. Observe the model. Fill the burette with distilled water; avoid air bubbles in stop cock; run out water into a beaker until the *lower* side of *meniscus* (Fig. 54) (curved surface) stands at 40.85 c.c.; estimate to tenths of a division; record this reading in your note-book; now run out water into a "graduate" until the latter is about half filled; take the reading on the "graduate"; how many $cm.^3$? Take the burette reading; how many $cm.^3$ did you run out? Compare readings. Which gives the more accurate measurement—burette or graduate? Why?

By means of a calibrated pipette (Fig. 55), introduce its nominal volume of water into a "graduate." Compare readings. Which is the more accurate? Why?

By use of the graduate, determine the approximate volumes of water which test tubes, beakers and flasks will hold. Make a record of data.

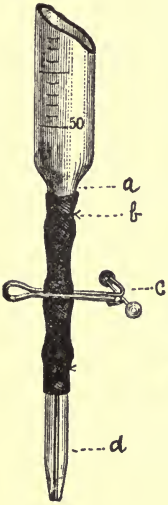

FIG. 52.—Burette Operated with Pinch-cock.

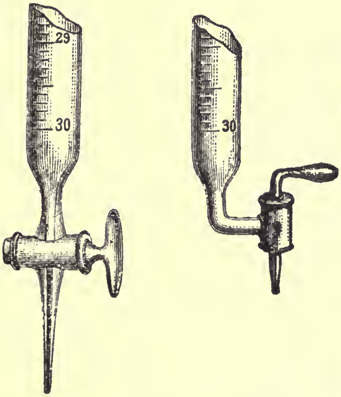

FIG. 53.—Burettes with Glass Stop-cocks.

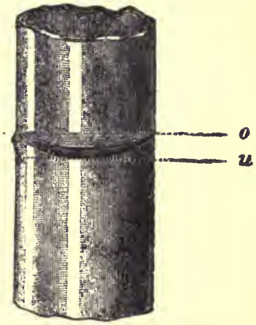

FIG. 54.—Meniscus.

By aid of burette, determine the volume occupied by a "drop" of water as delivered by your burette. *Hint.*—Run out ten to twenty drops. Make a record of exercise.

(*b*) Measure of temperature.

The mercury-glass therometer is ordinarily used in the laboratory. Note the possible maximum and minimum readings. Always observe this before using instrument. Some thermometers are made to read to only +60° C.; such a thermometer plunged into water boiling at any temperature above that registered on scale would undoubtedly be ruined. Never plunge the instrument into relative extremes of temperature.

Suspend the thermometer in a beaker of water which has presumably acquired the temperature of the laboratory. Remember the heat of the hand will affect the reading. It requires time for a thermometer to come to the temperature of a new environment—the thermometer is said to "lag." Gently tap the thermometer with finger before reading—this is to overcome "stiction." What is the temperature of the water in beaker on the Centigrade scale? Fahrenheit scale? Réaumur scale? Make a record of experiment.

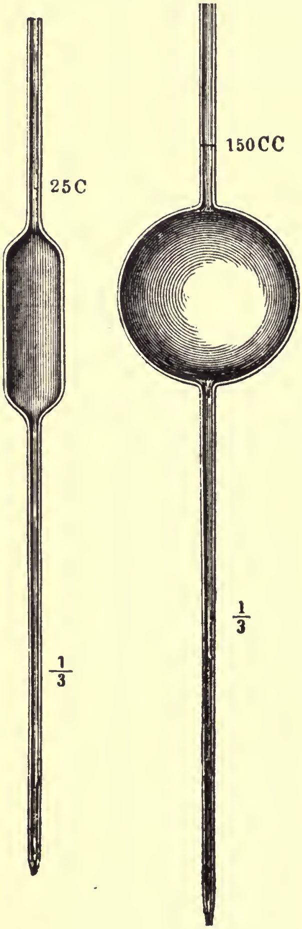

Fig. 55.—Pipettes.

The Beckmann thermometer for determining accurately small changes in temperature is frequently used. Consult the instructor with reference to its manipulation.

(*c*) Measures of weight.

The equal arm lever balance is the instrument most frequently used in the chemical laboratory for the determination of weight. The principle of this balance is embodied in two useful forms—the "platform" or "trip" balance and the so-called "analytical" balances (Fig. 56). Both kinds will be found in the laboratory. Examine them, the latter under the supervision of the assistant. The former is used in making those weighings where only an approximate accuracy is demanded; the latter are much more sensitive and accurate, and should be used only when the experiment is marked "Quant."

The balance and weights must be handled with care. Solids to be weighed must be placed first upon a piece of paper or a watch glass, never directly upon the pan. All objects must be perfectly clean and dry. The weights must be handled with forceps—not with the moist hand.

The general procedure when weighing with platform balances is as follows: find zero point of balance by allowing the beam to swing, noting whether the pointer makes equal excursions on either side of the zero mark; if it does not, correct defects by placing pieces of paper, etc., on the proper pan. This is called "counterpoising" a balance. In the future, when weighing, do not wait for pointer to come to rest at the zero point, simply add to or subtract weights from the proper pan until the vibrations on either side of zero point are of equal amplitude.

The assistant will instruct you as to the proper method of weighing with the "analytical" balances.

Note.—To avoid one of the commonest errors in weighing, count the values of the vacant places in the set, then *check* by counting the weights in the pan. Record on paper the value of the weights *as* you take them from the pan.

CALIBRATING BY WEIGHING.

Make a mark or paste a piece of gummed paper on the lower portion of the neck of a 50 $cm.^3$ Erlenmeyer flask. Weigh it first on the platform balances, then on the analytical balances. (Instructions.) Place flask on left pan. Record weights. Now fill flask to mark with water at 20° C. and weigh as before. Record weights. If a $cm.^3$ of water at 20° C. weighs .998 gram, what is the volume of flask when filled to mark? Which is buoyed up the most by air—flask and contents or weights? Is this a source of error?

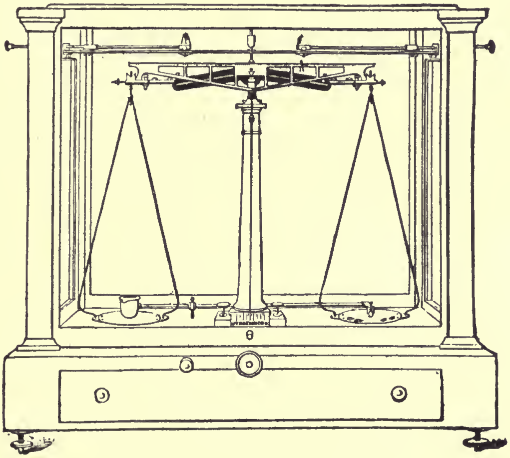

FIG. 56.—Chemical Balance.

PROBLEMS.

1. Express 10 cm. in millimeters, decimeters and kilometers.
2. Convert 115 in. into centimeters; 98 mm. into inches; 2 yd. into meters; 2 ft. into centimeters; 760 mm. into inches.
3. How many liters in 10 quarts? Quarts in 4 liters?
4. How many liters will a pneumatic trough hold, the dimensions of which are 15 in. x 20 in. x 25 in.?
5. Add 9 grm., 468 mg., 7 dg., and 5 cg., and express the sum in grams.
6. 10 kg. are equivalent to how many pounds? Convert 10 oz. into grams.

7. How many grams in 134.76 dg.? In 17,589 cg.? In 5.95 mg.?

8. How many cubic centimeters (cm.^{3}) in .5 l.? In .75 l.? In 95 dm.^{3}

9. Convert 32° Fahr. into a Centigrade reading. A Réaumur reading.

10. Repeat 9, using 212° Fahr.

11. A thermometer bearing a Fahrenheit scale registers a temperature of 72°. What would be the equivalent reading on the Centigrade scale? On the Réaumur Scale?

12. Convert 20° C. into an equivalent reading on the Fahr. scale. On the Réaumur scale.

13. The sp. gr. of concentrated sulphuric acid is 1.84, of nitric acid 1.4, and of hydrochloric acid 1.2. Calculate the weight of a liter of each acid.

14. How many cm.^{3} in 10 grm. of each of the above acids?

15. Alcohol (ethyl) at 15° C. has a density of .7937. What is the weight of one l. at 15° C. How many cm.^{3} in 20 grm.?

16. An empty flask has a weight of 96.75 grm.; when filled with water at 20° C. it has a weight of 596.30 grm. What is the capacity of the flask at 20° C.? *Hint.*—calculate the number of grams of water which the flask holds and multiply by the "correction factor," 1.0028. This factor corrects for the buoyant effect of the air in weighing, the density of water (.99823) at 20° C., and the cubical coefficient of expansion of glass (.000025). The "correction factor" for 19° C. is 1.0027. See Appendix. In standardizing volumetric apparatus the "correction factor" should always be used.

APPENDIX II.

NOTE.—The data contained in the following tables have been selected and arranged from various sources. Effort has been made to incorporate the results of the most recent investigations. In many instances it has been possible to give only approximate values.

The tables which have been most frequently consulted are: Landolt und Börnstein, Physikalisch-chemische Tabellen; Ostwald, Physico-chemical Measurements; Kohlrausch, Praktische Physik; Buchka, Physikalisch-chemische Tabellen der unorganischen Chemie; Watson, Practical Physics; Miller, Laboratory Physics; Smithsonian Physical Tables; Comey, Dictionary of Solubilities; Seidell, Solubilities of Inorganic and Organic Substances; J. Thomsen, Thermo-chemische Untersuchungen.

TABLE I.

Metric Measures with English Equivalents.

(a) Measures of Length.

1 Millimeter, mm. = .0393 inches.
1 Centimeter, cm. = 10 mm. = .3937 inches.
1 Decimeter, dm. = 10 cm. = 3.9371 inches.
1 Meter, m. = 10 dm. = 39.3708 inches.
1 Meter, m. = 3.2809 feet.
1 Meter, m. = 1.0936 yards.
1 Kilometer, Km. = 1000 m. = .6114 miles.

(b) Measures of Volume.

1 Cubic centimeter, cm.^{3} = .001 l. = .06103 cu. inches.
1 Cubic decimeter (liter), 1. = 1000 cm.^{3} = 61.227 cu. inches.
1 Liter = 2.1134 pints U.S. = 1.067 quarts U. S. = 0.26417 gallons U. S.
1 Cubic meter = 1000 l. = 35.317 cu. ft.

(c) Measures of Weight.

1 Milligram, mg. = .001 gram = .0154 grains.
1 Centrigram, cg. = .01 gram = .1543 grains.
1 Decigram, dg. = .1 gram = 1.5432 grains.
1 Gram, gm. = 15.432 grains = .0352 av. ounces.
1 Gram = .03216 troy ounces.
1 Kilogram (kilo) = 1000 grams = 2.2055 av. lbs.
1 Kilogram = 2.6803 troy lbs.

TABLE II.

English Measures with Metric Equivalents.

(a) Measures of Length.

1 Inch = 25.399 mm. = 2.539 centimeters.
1 Foot = 12 inches = .3048 meter.
1 Yard = 3 feet = .9144 meter.
1 Mile = 1700 yards = 5280 feet.
1 Mile = 1.609 kilometers = 1609.3 meters.

(b) Area.

1 Square inch = 6.4514 cm.^{2}
1 Square foot = 929.01 cm.^{2}
1 Square yard = 8361.1 cm.^{2}
1 Square yard = .83661 m.^{2}

(c) Contents.

1 Cubic inch = 16.386 cm.^{3}
1 Cubic foot = 28.316 liters.
1 Cubic yard- = 764.52 liters.
1 Cubic yard = about .76 m.^{3}

(d) Measures of Volume.

1 Pint = .47317 liter = 473.11 cubic centimeters.
1 Quart = .94634 liter = 946.22 cubic centimeters.
1 Gallon (U.S.) = 3.785 liters = 231 cubic inches.

(e) Apothecaries' Fluid Measure, U.S.

1 Minim = a drop (approx) = .0616 cubic centimeters.
1 Fluid dram = 60 minims = 3.6965 cubic centimeters.
1 Fluid ounce = 8 fluid drams = 29.572 cubic centimeters.
1 Pint = 16 fluid ounces = 473.11 cubic centimeters.

(f) Measures of Weight.

I. *(Avoirdupois.)*

1 Gram = 64.773 milligrams = 0.0648 grams.
1 Dram = 27.34 grains = 1.772 grams.
1 Ounce = 16 drams = 437.5 grains = 28.349 grams.
1 Pound = 16 ounces = 7000 grains = 453.59 grams.
1 Short ton = 2000 pounds = 907.17 kilograms.
1 Long ton = 2240 pounds = 1015.03 kilograms.

II. *(Troy.)*

1 Grain = 64.773 milligrams = .0648 grams.
1 Pennyweight = 24 grains = 1.555 grams.
1 Ounce = 20 pennyweights = 480 grains = 31.103 grams.
1 Pound = 12 ounces = 5760 grains = 373.242 grams.

III. *(Pharmacy or Apothecaries'.)*

1 Grain = 64.773 milligrams = .0648 grams.
1 Scruple = 20 grains = 1.296 grams.
1 Dram = 3 scruples = 60 grains = 3.888 grams.
1 Ounce = 8 drams = 480 grains = 31.1035 grams.
1 Pound = 12 ounces = 373.248 grams.

TABLE III.

Conversion of Thermometric Readings.

The temperatures mentioned in this book are expressed in terms of the Centigrade scale. There are three scales now in general use. They are:

I. Fahrenheit—F. Water freezes at 32°, boils at 212°.
II. Centigrade—C. Water freezes at 0°, boils at 100°.
III. Réaumur —R. Water freezes at 0°, boils at 80°.

To convert: F. to C. $\frac{F.^\circ - 32^\circ}{1.8} = C^\circ.$

or $\frac{5(F.^\circ - 32^\circ)}{9} = C^\circ.$

F. to R. $\frac{4(F.^\circ - 32^\circ)}{9} = R.$

C. to F. $(C. \times 1.8) + 32^\circ = F.^\circ.$

or $\frac{9\ C.^\circ + 32^\circ}{5} = F.^\circ$

R. to F. $\frac{9\ R.^\circ + 32^\circ}{4} = F.^\circ$

TABLE IV.

Corrections to Reduce Readings on Mercury-in-Glass Thermometers to the Normal Hydrogen Scale or Air Thermometer.

(For Jena Normal Glass, 16‴)*

Reading	0° C.	10° C.	20° C.	30° C.	40° C.	
Correction	0°.000	—0.055	—0.090	—0.109	—0.116	—0.109
Reading	50° C.	60 C.	70° C.	80° C.	90° C.	100° C.
Correction	—0°.109	—0.096	—0.076	—0.053	—0.027	0.000

*From tables published by Grützmacher in Wied. Annalen (1899) p. 769.

TABLE V. DENSITY OF WATER.*

(At the Temperature "*t*" on the Normal Hydrogen Scale)

Degrees C.	Tenths.									
	0	1	2	3	4	5	6	7	8	9
0°	0·99987	87	88	89	89	90	90	91	92	92
1	93	93	94	94	95	95	95	96	96	97
2	97	97	97	$\underline{98}$	$\underline{98}$	$\underline{99}$	$\underline{99}$	$\underline{99}$	$\underline{99}$	$\underline{99}$
3	99	99	99	00	00	00	00	00	00	00
4	1·00000	00	00	00	00	00	00	00	00	00
5	0·99999	99	99	99	98	98	98	98	97	97
6	97	97	96	96	95	95	95	94	94	93
7	93	93	92	92	91	90	90	89	89	88
8	88	87	86	86	85	84	84	83	82	82
9	81	80	79	79	78	77	76	75	74	74
10	73	72	71	70	69	68	67	66	65	64
11	63	62	61	60	59	58	57	56	55	54
12	53	51	50	49	48	47	45	44	43	42
13	40	39	38	37	35	34	33	31	30	29
14	27	26	24	23	22	20	19	17	16	14
15	13	11	10	08	06	05	03	02	00	$\overline{99}$
16	0·99897	95	94	92	90	89	87	85	84	82
17	80	78	77	75	73	71	70	68	66	64
18	62	60	59	57	55	53	51	49	47	45
19	43	41	39	37	35	33	31	29	27	25
20	23	21	19	17	15	13	11	08	06	04
21	02	00	$\overline{98}$	$\overline{95}$	$\overline{93}$	$\overline{91}$	$\overline{89}$	$\overline{86}$	$\overline{84}$	$\overline{82}$
22	0·99780	77	75	73	71	68	66	64	61	59
23	56	54	52	49	47	45	42	40	37	35
24	32	30	27	25	22	20	17	15	12	10
25	07	05	02	$\overline{99}$	$\overline{97}$	$\overline{94}$	$\overline{92}$	$\overline{89}$	$\overline{86}$	$\overline{84}$
26	0·99681	78	76	73	70	67	65	62	59	57
27	54	51	48	46	43	40	37	34	32	29
28	26	23	20	17	15	12	09	06	03	00
29	0·99597	94	91	88	85	82	79	76	73	70
30	67	64	61	58	55	52	49	46	43	40
31	37	34	$\underline{31}$	$\underline{27}$	$\underline{24}$	$\underline{21}$	$\underline{18}$	$\underline{15}$	$\underline{12}$	$\underline{08}$
32	05	02	99	96	92	89	86	83	79	76
33	0·99473	70	66	63	60	56	53	50	46	43
34	40	36	33	30	26	23	20	16	13	09
35	06	02	$\overline{99}$	$\overline{95}$	$\overline{92}$	$\overline{89}$	$\overline{85}$	$\overline{82}$	$\overline{78}$	$\overline{75}$

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*Watson.

TABLE VI.

VOLUME OF ONE GRAM OF WATER.*

(Thiesen, Scheel, and Diesselhorst, in Wiss. Abh. d. Phys. Tech. Reichsanstalt, Vol. II, 1895; Vol. III, 1900; and Vol. IV, 1904.)

Temperature.	0	1	2	3	4	5	6	7	8	9
0	1·00013	007	003	001	000	001	003	007	012	019
10	027	037	048	060	073	087	103	120	138	157
20	177	199	221	244	268	294	320	347	376	405
30	435	466	497	530	563	598	633	669	706	743
40	782	821	861	901	943	985	$\overline{028}$	$\overline{072}$	$\overline{116}$	$\overline{162}$
50	1·01207	254	301	349	398	448	498	548	600	652
60	705	758	812	867	923	979	$\overline{036}$	$\overline{093}$	$\overline{151}$	$\overline{210}$
70	1·02270	330	390	452	514	576	639	703	768	833
80	899	965	$\overline{032}$	$\overline{099}$	$\overline{168}$	$\overline{237}$	$\overline{306}$	$\overline{376}$	$\overline{447}$	$\overline{518}$
90	1·03590	663	736	810	884	959	$\overline{035}$	$\overline{111}$	$\overline{188}$	$\overline{265}$
100	1·04343	422	501							

*1 gram of ice has a volume of 1.09008 cm.³

TABLE VII.

DENSITY OF MERCURY.*

(At the Temperature (t) on the Normal Hydrogen Scale.)

t°	Density	t°	Density	t°	Density	t°	Density	t°	Density	t°	Density
0	13·5950										
1	·5925	6	·5802	11	·5679	16	·5556	21	·5433	26	·5310
2	·5901	7	·5777	12	·5654	17	·5531	22	·5408	27	·5286
3	·5876	8	·5753	13	·5629	18	·5507	23	·5384	28	·5261
4	·5851	9	·5728	14	·5605	19	·5482	24	·5359	29	·5237
5	13·5827	10	13·5703	15	13·5581	20	13·5457	25	13·5335	30	13·5212

*Thiesen, Guillaume, International Congress of Physics, Paris, 1900.

TABLE VIII. BAROMETRIC CORRECTIONS.

(a) REDUCTION OF BAROMETER READINGS TO 0°. CORRECTIONS FOR THE EXPANSION OF THE MERCURY AND THE SCALE.

The following corrections* are to be subtracted.

Temperature.	BRASS SCALE.					GLASS SCALE.				
	OBSERVED HEIGHT.					OBSERVED HEIGHT.				
C.°	740	750	760	770	780	740	750	760	770	780
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
1	·12	·12	·12	·13	·13	·13	·13	·13	·13	·13
2	·24	·25	·25	·25	·25	·26	·26	·26	·27	·27
3	·36	·37	·37	·38	·38	·38	·39	·39	·40	·41
4	·48	·49	·50	·50	·51	·51	·52	·53	·53	·54
5	·60	·61	·62	·63	·64	·64	·65	·66	·67	·68
6	·72	·73	·74	·75	·76	·77	·78	·79	·80	·81
7	·85	·86	·87	·88	·89	·90	·91	·92	·93	·95
8	·97	·98	·99	1·01	1·02	1·02	1·04	1·05	1·07	1·08
9	1·09	1·10	1·12	1·13	1·15	1·15	1·17	1·18	1·20	1·21
10	1·21	1·22	1·24	1·26	1·27	1·28	1·30	1·31	1·33	1·35
11	1·33	1·35	1·36	1·38	1·40	1·41	1·43	1·45	1·46	1·48
12	1·45	1·47	1·49	1·51	1·53	1·53	1·56	1·58	1·60	1·62
13	1·57	1·59	1·61	1·63	1·65	1·66	1·69	1·71	1·73	1·75
14	1·69	1·71	1·73	1·76	1·78	1·79	1·81	1·84	1·86	1·89
15	1·81	1·83	1·86	1·88	1·91	1·92	1·94	1·97	2·00	2·02
16	1·93	1·96	1·98	2·01	2·03	2·05	2·07	2·10	2·13	2·16
17	2·05	2·08	2·10	2·13	2·16	2·17	2·20	2·23	2·26	2·29
18	2·17	2·20	2·23	2·26	2·29	2·30	2·33	2·36	2·39	2·43
19	2·29	2·32	2·35	2·38	2·41	2·43	2·46	2·49	2·53	2·56
20	2·41	2·44	2·47	2·51	2·54	2·56	2·59	2·62	2·66	2·69
21	2·53	2·56	2·60	2·63	2·67	2·68	2·72	2·76	2·79	2·83
22	2·65	2·69	2·72	2·76	2·79	2·81	2·85	2·89	2·92	2·96
23	2·77	2·81	2·84	2·88	2·92	2·94	2·98	3·02	3·06	3·10
24	2·89	2·93	2·97	3·01	3·05	3·06	3·11	3·15	3·19	3·23
25	3·01	3·05	3·09	3·13	3·17	3·19	3·23	3·28	3·32	3·36
26	3·13	3·17	3·21	3·26	3·33	3·32	3·36	3·41	3·45	3·50
27	3·25	3·29	3·34	3·38	3·42	3·45	3·49	3·54	3·59	3·63
28	3·37	3·41	3·46	3·51	3·55	3·57	3·62	3·67	3·72	3·77
29	3·49	3·54	3·58	3·63	3·68	3·70	3·75	3·80	3·85	3·90
30	3·61	3·66	3·71	3·75	3·80	3·83	3·88	3·93	3·98	4·03
31	3·73	3·78	3·83	3·88	3·93	3·95	4·01	4·06	4·11	4·17
32	3·85	3·90	3·95	4·00	4·05	4·08	4·14	4·19	4·25	4·30
33	3·97	4·02	4·07	4·13	4·18	4·21	4·26	4·32	4·38	4·43
34	4·09	4·14	4·20	4·25	4·31	4·33	4·39	4·45	4·51	4·57
35	4·21	4·26	4·32	4·38	4·43	4·46	4·52	4·58	4·65	4·71

*The coefficient of expansion of mercury is 0.0001813. If β is the coefficienct of expansion of the scale, an amount equal to (0.0001813-β)ht must be subtracted from the observed height (h) to obtain the reading if the scale and mercury were reduced to 0° C. (Glass, β=.000009; brass, β=.00002; steel, β=.00012.)

(b) CORRECTION FOR VARIATION IN g.

Latitude	730	740	750	760	770	780	790
	mm.	mm.	mm.	mm.	mm.	mm.	mm.
45°	0	0	0	0	0	0	0
40° or 50°	·32	·33	·33	·34	·35	·35	·35
35° or 55°	·65	·66	·66	·67	·68	·69	·70

TABLE IX.

REDUCTION TO VACUUM OF WEIGHINGS MADE IN AIR.

If a body of density (D) has an apparent weight of (G) grams when weighed in in the air, its weight reduced to vacuum is G + Gk grams. k is computed for air of density .0012 and for brass weights of density 8.4, and platinum weights, 21.5.

$$G_o = G \left(1 + \frac{.0012}{D} - \frac{.0012}{8.4} \right) = G\,(1 + k)$$

Density of Body. *D.*	Correction in Milligrams.	
	Brass Weights. *d.* = 8·4.	Platinum Weights. *d.* = 21·5.
	k.	k.
0·50	+2·26	+2·34
·55	2·04	2·13
·60	1·86	1·94
·65	1·70	1·79
·70	1·57	1·66
·75	1·46	1·55
·80	1·36	1·44
·85	1·27	1·36
·90	1·19	1·28
·95	1·12	1·21
1·0	1·06	1·14
1·1	·95	1·04
1·2	·86	·94
1·3	·78	·87
1·4	·71	·80
1·5	·66	·75
1·6	·61	·69
1·7	·56	·65
1·8	·52	·62
1·9	·49	·58
2·0	·46	·54
2·5	·34	·43
3·0	·26	·34
3·5	·20	·29
4·0	·16	·24
5·0	·10	·19
6·0	·06	·14
8·0	+·01	·09
10·0	—·02	·06
15·0	—·06	·03
20·0	—·08	·004

TABLE X.

Volume of a Glass Vessel at Various Temperatures.

Correction Factors for Calibrating Glass Vessels.

In calibrating glass vessels by weighing them filled with water (or mercury) at a known t°, it is necessary to correct for the effect of temperature on the density of the liquid, the buoyant effect of the air, and the effect of temperature on the volume of the flask. To ascertain the true *volume* (in $cm.^3$) of a flask filled with distilled water at a temperature of 20° C., multiply its apparent weight (in grams) by 1.0028. These "factors" assume the use of brass weights in air of density .0012 (approx.), and that the coefficient of cubical expansion of glass is .000025.

t.	Volume-Water.	*t.*	Volume-Mercury.
°	ccm.	°	ccm.
5	1.001 49	5	0.073 647
6	.001 49	6	.073 658
7	.001 50	7	.073 669
8	.001 53	8	.073 681
9	.001 57	9	.073 693
10	1.001 63	10	0.073 704
11	.001 70	11	.073 716
12	.001 78	12	.073 727
13	.001 88	13	.073 739
14	.001 99	14	.073 750
15	1.002 10	15	0.073 762
16	.002 23	16	.073 773
17	.002 38	17	.073 785
18	.002 53	18	.073 797
19	.002 70	19	.073 808
20	1.002 87	20	0.073 820
21	.003 06	21	.073 831
22	.003 26	22	.073 843
23	.003 47	23	.073 854
24	.003 69	24	.073 866
25	1.003 92	25	0.073 877
26	.004 15	26	.073 889
27	.004 39	27	.073 900
28	.004 65	28	.073 912
29	.004 92	29	.073 923
30	1.005 19	30	0.073 935

TABLE XI.

Vapor Tension of Water.

Between 0° C and 35° C.

Degree.	VAPOR TENSION IN MILLIMETRES OF MERCURY.									
	Tenths.									
	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	4·57	4·60	4·64	4·67	4·70	4·74	4·77	4·80	4·84	4·87
1	4·91	4·94	4·98	5·02	5·05	5·09	5·12	5·16	5·20	5·23
2	5·27	5·31	5·35	5·39	5·42	5·46	5·50	5·54	5·58	5·62
3	5·66	5·70	5·74	5·78	5·82	5·86	5·94	5·94	5·99	6·03
4	6·07	6·11	6·15	6·20	6·24	6·28	6·33	6·37	6·42	6·46
5	6·51	6·55	6·60	6·64	6·69	6·74	6·78	6·83	6·88	6·92
6	6·97	7·02	7·07	7·12	7·17	7·22	7·26	7·31	7·36	7·42
7	7·47	7·52	7·57	7·62	7·67	7·72	7·78	7·83	7·88	7·94
8	7·99	8·05	8·10	8·15	8·21	8·27	8·32	8·38	8·43	8·49
9	8·55	8·61	8·66	8·72	8·78	8·84	8·90	8·96	9·02	9·08
10	9·14	9·20	9·26	9·32	9·39	9·45	9·51	9·58	9·64	9·70
11	9·77	9·83	9·90	9·96	10·03	10·09	10·16	10·23	10·30	10·36
12	10·43	10·50	10·57	10·64	10·71	10·78	10·85	10·92	10·99	11·07
13	11·14	11·21	11·28	11·36	11·43	11·50	11·58	11·66	11·73	11·81
14	11·88	11·96	12·04	12·12	12·19	12·27	12·35	12·43	12·51	12·59
15	12·67	12·76	12·84	12·92	13·00	13·09	13·17	13·25	13·34	13·42
16	13·51	13·60	13·68	13·77	13·86	13·95	14·04	14·12	14·21	14·30
17	14·40	14·49	14·58	14·67	14·76	14·86	14·95	15·04	15·14	15·23
18	15·33	15·43	15·52	15·62	15·72	15·82	15·92	16·02	16·12	16·22
19	16·32	16·42	16·52	16·63	16·73	16·83	16·94	17·04	17·15	17·26
20	17·36	17·47	17·58	17·69	17·80	17·91	18·02	18·13	18·24	18·35
21	18·47	18·58	18·69	18·81	18·92	19·04	19·16	19·27	19·39	19·51
22	19·63	19·75	19·87	19·99	20·11	20·24	20·36	20·48	20·61	20·73
23	20·86	20·98	21·11	21·24	21·37	21·50	21·63	21·76	21·89	22·02
24	22·15	22·29	22·42	22·55	22·69	22·83	22·96	23·10	23·24	23·38
25	23·52	23·66	23·80	23·94	24·08	24·23	24·37	24·52	24·66	24·81
26	24·96	25·10	25·25	25·40	25·55	25·70	25·86	26·01	26·16	26·32
27	26·47	26·63	26·78	26·94	27·10	27·26	27·42	27·58	27·74	27·90
28	28·07	28·23	28·39	28·56	28·73	28·89	29·06	29·23	29·40	29·57
29	29·74	29·92	30·09	30·26	30·44	30·62	30·79	30·97	31·15	31·33
30	31·51	31·69	31·87	32·06	32·24	32·43	32·61	32·80	32·99	33·18
31	33·37	33·56	33·75	33·94	34·14	34·33	34·53	34·72	34·92	35·12
32	35·32	35·52	35·72	35·92	36·13	36·33	36·54	36·74	36·95	37·16
33	37·37	37·58	37·79	38·00	38·22	38·43	38·65	38·87	39·08	39·30
34	39·52	39·74	39·97	40·19	40·41	40·64	40·86	41·09	41·32	41·55
35	41·78	42·02	42·25	42·48	42·72	42·96	43·19	43·43	43·67	43·92

TABLE XII.

VAPOR TENSION OF WATER.

From 0° C. to 100° C.

Temp.	Tension mm.	Temp.	Tension mm.	Temp.	Tension mm.	Temp.	Tension mm.
0	4.569	25	23.517	50	91.98	75	288.76
1	4.909	26	24.956	51	96.66	76	301.09
2	5.272	27	26.471	52	101.55	77	313.85
3	5.658	28	28.065	53	106.65	78	327.05
4	6.069	29	29.744	54	111.97	79	340.73
5	6.507	30	31.51	55	117.52	80	354.87
6	6.972	31	33.37	56	123.29	81	369.51
7	7.466	32	35.32	57	129.31	82	384.64
8	7.991	33	37.37	58	135.58	83	400.29
9	8.548	34	39.52	59	142.10	84	416.47
10	9.140	35	41.78	60	148.88	85	433.19
11	9.767	36	44.16	61	155.95	86	450.47
12	10.432	37	46.65	62	163.29	87	468.32
13	11.137	38	49.26	63	170.02	88	486.76
14	11.884	39	52.00	64	178.86	89	505.81
15	12.674	40	54.87	65	187.10	90	525.47
16	13.510	41	57.87	66	195.67	91	545.77
17	14.395	42	61.02	67	204.56	92	566.71
18	15.330	43	64.31	68	213.79	93	588.83
19	16.319	44	67.76	69	223.37	94	610.64
20	17.363	45	71.36	70	233.31	95	633.66
21	18.466	46	75.13	71	243.62	96	657.40
22	19.630	47	79.07	72	254.30	97	681.88
23	20.858	48	83.19	73	265.38	98	707.13
24	22.152	49	87.49	74	276.87	99	733.16

*Taken from Ostwald's Manual of Physico-Chemical Measurements.

TABLE XIII.

VAPOR PRESSURE OF MERCURY.

(Ramsay and Young,—Jour. of the Chem. Soc., 1886, p. 37.)

Temperature.	Vapor Pressure. mm.	Temperature.	Vapor Pressure. mm.
40°	0·008	180°	8·535
50	·015	190	12·137
60	·029	200	17·015
70	·052	210	23·482
80	·092	220	31.957
90	·160	230	42·919
100	·270	240	56·919
110	·445	250	74·592
120	·719	260	96·661
130	1·137	270	123·905
140	1·763	280	157·378
150	2·684	290	198·982
160	4·013	300	246·704
170	5·904		

TABLE XIV.

BOILING TEMPERATURE (*t*) OF WATER AT BAROMETRIC PRESSURE (*b*).
(After Regnault.)

b	*t*	*b*	*t*	*b*	*t*	*b*	*t*	*b*	*t*
680	96.92°	700	97.72°	720	98.49°	740	99.26°	760	100.00°
681	.96	01	.75	21	.53	41	.29	61	.04
682	97.00	02	.79	22	.57	42	.33	62	.07
683	.04	03	.83	23	.61	43	.37	63	.11
684	.08	04	.87	24	.65	44	.41	64	.15
685	.12	05	.91	25	.69	45	.44	65	.18
686	.16	06	.95	26	.72	46	.48	66	.22
687	.20	07	97.99	27	.76	47	.52	67	.26
688	.24	08	98.03	28	.80	48	.56	68	.29
689	.28	09	.07	29	.84	49	.59	69	.33
690	.32	710	.11	730	.88	750	.63	770	.36
691	.36	11	.15	31	.92	51	.67	71	.40
692	.40	12	.19	32	.95	52	.70	72	.44
693	.44	13	.22	33	98.99	53	.74	73	.47
694	.48	14	.26	34	99.03	54	.78	74	.51
695	.52	15	.30	35	.07	55	.82	75	.55
696	.56	16	.34	36	.11	56	.85	76	.58
697	.60	17	.38	37	.14	57	.89	77	.62
698	.64	18	.42	38	.18	58	.93	78	.65
699	.68	19	.46	39	.22	59	.96	79	.69
700	97.72	720	98.49	740	99.26	760	100.00	780	100.72

TABLE XV.

BOILING TEMPERATURE (*t*) OF WATER AT A PRESSURE OF (*a*) ATMOSPHERES.
(Regnault.)

t	*a*	*t*	*a*
100° C.	1.000	180° C.	9.929
121	2.025	189	12.125
134	3.008	199	15.062
144	4.000	213	19.997
152	4.971	225	25.125
159	5.966	239	27.534
171	8.036		

TABLE XVI. PHYSICAL CONSTANTS.

(Travers.)

	Absolute boiling point.	Absolute melting point.	Absolute critical point. *	Critical pressure (mm.).	Density at boiling point.	Color of liquid.
	°	°	°			
Hydrogen	20	16	35	11,600	0.06	Colorless
Oxygen	90.5	below 50	154	44,080	1.131	Bluish
Nitrogen (chemical)	77.54	60	124	20,930	0.791	Colorless
Nitrogen (atmospheric)	77.50	60	......	......	......	"
Carbon monoxide	83.0	66	137	25,400	......	"
Carbon dioxide	193	......	304	55,000	......	"
Nitric oxide	123.1	......	179?	54,000?	......	"
Nitrous oxide	183.2	170.3	310.0	......	......	"
Methane	108.3	......	191	42,400	0.416	"
Ethane	180	below 120	305	38,100	......	"
Propane	228	......	370	33,440	......	"
Ethylene	169.5	104	282	44,080	0.571	"
Acetylene	190.5	......	308	46,375	......	"
Methyl chloride	249.3	......	416	41,000	......	"
Sulphur dioxide	263	......	428.4	60,000	......	"
Fluorine	186	......	......	......	1.11	Yellowish
Chlorine	239.6	......	......	......	1.507	Colorless
Hydrogen sulphide	211.5	......	373	69,900	......	"
Hydrogen phosphide	188	......	......	......	......	"
Ammonia	234.5	197.5	404	85,900	......	"
Helium	below 20	......	......	......	......	"
Neon	30–40	......	below 65	......	......	"
Argon	86.90	......	155.6	40,200	1.212	"
Krypton	121.33	......	210.5	41,240	2.155	"
Xenon	163.9	......	287.8	43,500	3.52	"

*Critical temperature of water 370°–390° C.

TABLE XVII.

COMPOSITION OF THE AIR BY VOLUME.

(Average.)

	Vols. per 1000.
Nitrogen	769.5000
Oxygen	206.5940
Aqueous vapor	14.0000
Argon *	9.3700
Carbon dioxide	0.3360
Hydrogen	0.1900
Ammonia	0.0080
Ozone	0.0015
Nitric acid	0.0005
	1000.0000

*The other four elements of the argon group constitute about .012 parts in a 1000. Small quantities of solids are also present, e. g., ammonium nitrate, ammonium carbonate, sodium chloride, dust, etc.

TABLE XVIII.

DIFFUSION OF GASES.

(Graham, 1834)

Gas.	Density (air = 1)	Square root of density	$\frac{1}{\sqrt{\text{Density}}}$	Actual velocity of diffusion by experiment
Hydrogen	0·06926	0·2632	3·7794	3·83
Marsh gas	0·559	0·7476	1·3375	1·344
Steam	0·6235	0·7896	1·2664	......
Carbon monoxide	0·9678	0·9837	1·0165	1·1149
Nitrogen	0·9713	0·9856	1·0147	1·0143
Ethylene	0·978	0·9889	1·0112	1·0191
Nitric oxide	1·039	1·1096	0·9808	......
Oxygen	1·1056	1·0515	0·9510	0·9487
Sulphuretted hydrogen	1·1912	1·0914	0·9162	0·95
Nitrous oxide	1·527	1·2357	0·8092	0·82
Carbon dioxide	1·52901	1·2365	0·8087	0·812
Sulphur dioxide	2·247	1·4991	0·6671	0·68

TABLE XIX.

Specific Heat—Atomic Heat.

Dulong-Petit's Law. $A = \frac{6.4.}{S}$

Elements.		S*	A	S x A
Lithium	Li	0,941	7.	6.6
Beryllium	Be	0,408	9.	3.7
Boron (amorphous)	B	0,254	11.	2.8
Graphite	C	0,174	12.	2.1
Diamond		0,143		1.7
Sodium	Na	0,239	23.	6.7
Magnesum	Mg	0,245	24.4	5.9
Aluminum	Al	0,202	27.	5.5
Silicon (cryst.)	Si	0,165	28.	4.6
Phosphorus	P	0,189	31.	5.9
Sulphur (rhombic)	S	0,178	32.	5.7
Potassium	K	0,166	39.	6.5
Calcium	Ca	0,170	40.	6.8
Chromium	Cr	0,100	52.	5.2
Manganese	Mn	0,122	55.	6.7
Iron	Fe	0,112	55.9	6.3
Cobalt	Co	0,107	59.	6.3
Nickel	Ni	0,108	58.7	6.4
Copper	Cu	0,093	63.6	5.9
Zinc	Zn	0,093	65.4	6.1
Gallium	Ga	0,079	70.	5.5
Germanium	Ge	0,057	72.5	5.4
Arsenic (cryst.)	As	0,082	75.	6.2
Selenium (cryst.)	Se	0,080	79.2	6 4
Bromine (solid)	Br	0,084	79.7	6.7
Zirconium	Zr	0,066	90.6	6.0
Molybdenum	Mo	0,072	96.	6.9
Ruthenium	Ru	0,061	101.7	6.3
Rhodium	Rh	0,058	103.	6.0
Palladium	Pd	0,059	106.5	6.3
Silver	Ag	0,056	107.9	6.0
Cadmium	Cd	0,054	112.4	6.0
Indium	In	0,057	115.	6.4
Tin	Sn	0,054	119.	6.4
Antimony	Sb	0,052	120.2	6.2
Tellurium	Te	0,047	127.6	6.0
Iodine	I	0,054	126.9	6.8
Lanthanum	La	0,045	138.9	6.2

* Richter.

TABLE XIX.—Continued.

Elements.		S*	A	S x A
Cerium	Ce	0,045	140.2	6.2
Didymium†	Di	0,045	142.	6.4
Tungsten	W	0,033	184.	6.1
Osmium	Os	0,031	191.	6.1
Iridium	Ir	0,032	193.	6.3
Platinum	Pt	0,032	194.8	6.3
Gold	Au	0,032	197.2	6.3
Mercury (solid)	Hg	0,032	200.	6.4
Thallium	Tl	0,033	204.1	6.7
Lead	Pb	0,031	206.9	6.4
Bismuth	Bi	0,030	208.	6.3
Thorium	Th	0,027	232.5	6.4
Uranium	Ur	0,027	238.5	6.4

* Richter.

† Didymium = Pr. and Nd.

TABLE XX.

Heat of Formation.*

(Arranged from Thomsen's Thermo-chemische Untersuchungen.)

(*a*) *Chlorides, Bromides and Iodides.*

Formula.	Chlorides.		Bromides.		Iodides.	
	(anhyd) †	(aq.) ‡	(anhyd.)	(aq.)	(anhyd.)	(aq.)
AlR_3	160900	237700	129600	204900	70300	159300
SbR_3	91400	—	—	—	—	—
AsR_3	71400	—	47100	—	12600	—
BaR_2	194200	196300	169400	174400	—	144000
BiR_3	90600	—	—	—	—	—
CaR_2	183800	201200	154900	179400	107600	14900
CdR_2	93200	96200	75200	75600	48900	47900
CoR_2	76400	94800	—	72900	—	42500
CuR	32800	—	24900	—	16200	—
CuR_2	51600	62700	32500	40800	—	—
AuR	5800	—	−100	—	−5500	—
AuR_3	22800	27200	8800	−5000	—	—
$H\,R$	22000	39300	8400	28300	−6300	13100
FeR_2	82000	99900	—	78000	—	47600
FeR_3	96000	127700	—	—	—	—
PbR_2	82700	75900	64400	54400	39600	—
LiR	93800	101300	79900	91300	61200	76100
MgR_2	151000	186900	—	165000	—	134600
MnR_2	111900	128000	—	106100	—	75700
Hg_2R_2	65200	—	50900	—	31100	—
HgR_2	54500	51200	4190	—	25600	—
NiR_2	74000	93700	—	71800	—	41400
$K\,R$	105600	101200	95300	90200	80100	75000
AgR	29300	—	27700	—	13800	—
NaR	97600	96500	85700	85600	69100	70300
SrR_2	184500	195700	157700	173800	—	143400
TlR	48500	38400	41400	—	30100	—
TlR_3	—	89000	—	56400	—	10500
SnR_2	80800	81100	—	—	—	—
SnR_4	127200	157000	—	—	—	—
ZnR_2	97200	112800	75900	90900	49200	60500

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* Smoothed values have been taken.

† Compound in usual state of aggregation.

‡ Compound formed in dilute aqueous solution.

(*b*) *Sulphates, Nitrates and Carbonates.*

Formula.	Sulphates.		Formula.	Nitrates.	
	(anhyd.)	(aq.)		(anhyd.)	(aq.)
$Al_2(SO_4)_3$	—	878900	—	—	—
$BaSO_4$	337500	—	$Ba(NO_3)_2$	219800	215200
$CaSO_4$	33240	336800	$Ca(NO_3)_2$	216700	220700
$CdSO_4$	221100	231800	$Cd(NO_3)_2$	121200	115800
$CoSO_4$	233900	230400	$Co(NO_3)_2$	119300	114300
$CuSO_4$	182500	198300	$Cu(NO_3)_2$	92900	82200
H_2SO_4	192900	210700	HNO_3	41600	49100
$FeSO_4.7H_2O$	240000	235600	$Fe(NO_3)_2$	—	119500
$PbSO_4$	216200	—	$Pb(NO_3)_2$	105500	97900
Li_2SO_4	334100	340100	$LiNO_3$	111600	112200
$MgSO_4$	302200	323000	$Mg(NO_3)_2$	210570	206300
$MnSO_4$	249800	263500	$Mn(NO_3)_2$	—	147500
			$HgNO_3$	—	38900
			$Hg(NO_3)_2$	—	67100
$NiSO_4$	—	229300	$Ni(NO_3)_2$	120760	113200
K_2SO_4	344500	337200	KNO_3	119400	111400
Ag_2SO_4	167200	162700	$AgNO_3$	28700	23300
Na_2SO_4	328500	32900	$NaNO_3$	111200	106200
$SrSO_4$	330800	—	$Sr(NO_3)_2$	219800	215200
Tl_2SO_4	221000	212700	$TlNO_3$	58100	48100
$ZnSO_4$	230000	248000	$Zn(NO_3)_2$	138200	132300
$BaCO_3$	281300	—	$CaCO_3$	269200	—
$CdCO_3$	181900	—	$PbCO_3$	168200	—
$MnCO_3$	210800	—	K_2CO_3	279500	286000
Ag_2CO_3	121300	—	Na_2CO_3	271000	276500
$SrCO_3$	279600	—	—	—	—

(*c*) *Oxides, Hydroxides and Sulphides.*

Formula.	Oxides.		Formula.	Hydroxides.	
	(anhyd.)	(aq.)		(anhyd.)	(aq.)
As_2O_3	154600	147000	$Al(OH)_3$	296900	—
BaO	130400	158200	$Ba(OH)_2$	216300	226600
CaO	14500	163300	Cd,O,H_2O	65700	—
CuO	37100	—	Ca,O_2,H_2	—	231700
Cu_2O	40800	—	Co,O,H_2O	63400	—
H_2O			$Au_2O_3,3H_2O$	13200	—
(vapor)	57061	cal.	Fe,O,H_2O	68200	—
(liquid)	68360	cal.	$Fe_2,O_3,3H_2O$	191100	—
20° C.					
PbO	50300	—	Li,O,H	—	117400
Li_2O	—	166500	Mg,O,H_2O	148900	—
HgO	22000	—	Mn,O,H_2O	94700	—
Hg_2O	24860	—	Ni,O,H_2O	60800	—
K_2O	99100	164500	K,O,H	103900	116400
Ag_2O	5900	—	$NaOH$	102000	111800
Na_2O	99800	155200	Sr,O_2,H_2	216400	226100
SrO	128400	157700	Zn,O,H_2O	82600	—
Al_2S_3	124400	—			
BaS	99500	107100	BaS_2H_2	—	124100
CaS	92000	110200	CaS_2H_2	—	125300
CuS	10000	—	CdS,nH_2O	32400	—
Cu_2S	18200	—	FeS,nH_2O	21800	—
H_2S	2700	7300	Co,S,nH_2O	19700	—
PbS	18400	—	Ni,S,nH_2O	17400	—
Li_2S	—	113200	$LiSH$	—	64100
MgS	79600	110000 ?	MgS_2H_2	—	110800
HgS	16800	—	ZnS,nH_2O	39600	—
K_2S	102400	111300	KSH	—	63100
Ag_2S	33000	—			
Na_2S	88400 ?	101900	$NaSH$	55000	58500
SrS	99200 ?	104700	SrS_2H_2	—	119700

TABLE XXI. SOLUBILITIES.

W = soluble in water; (w) = slightly soluble in water but soluble in acids (HCl, HNO_3, or aqua regia.) A = soluble in acids; (a) = slightly soluble in acids; I = insoluble in acids.

	Acetates.	Arsenates.	Arsenites.	Borates.	Bromides.	Carbonates.	Chlorates.	Chlorides.	Chromates.	Cyanides.	Ferricyanides.	Ferrocyanides.	Fluorides.	Hydroxides.	Iodides.	Nitrates.	Oxalates.	Oxides.	Phosphates.	Silicates.	Sulphates.	Sulphides.	Tartrates.
$\mathrm{Al'''}$	W	A		A	W		W	W					W	A	W	W	A	A	A	(a)	W	A	W
$\mathrm{NH'_4}$	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W		W		W	W	W
$\mathrm{Sb'''}$	W	A	A		(w)			(w)*	A				W		(w)		A	A	(w)		(w)	A	A
$\mathrm{Ba''}$	W	A	A	A	W	A	W	W	A	(w)	(w)	(w)	(a)	W	W	W	A	W	A	A	I	W	A
$\mathrm{Bi'''}$	W	A		A	(w)	A	W	(w)*	A	(w)		I	W	A	A	W*	A	A	A		W	A	A
$\mathrm{Cd''}$	W	A		(w)	W	A	W	W	A	A	A		(w)	A	W	W	A	A	A	A	W	A	(w)
$\mathrm{Ca''}$	W	A	A	A	W	A	W	W	(w)	W	W	W	(a)	(w)	W	W	A	(w)	A	A	(a)	W	A
$\mathrm{Cr'''}$	W	A		A	W		W	W	A	A			W	A	W	W	(w)	A	A	A	W	A	W
$\mathrm{Co''}$	W	A	A	A	W	A	W	W	A	(a)	I	I	(w)	A	W	W*	A	A	A	A	W	A	W
$\mathrm{Cu''}$	W	A	A	A	W	A	W	W	W	A	I	I	A	A	W	W	A	A	A	A	W	A	W
$\mathrm{Au'''}$					W		W	W		A				A	A	W		A	A			A	
$\mathrm{H'}$	W	W		W	W		W	W		W	W	W	W	W	W	W	W	W	W	W	W	(w)	W
$\mathrm{Fe''}$	W	A	A	A	W	A	W	W		(a)	I	I	(w)	A	W	W	A	A	A	A	W	A	(w)
$\mathrm{Fe'''}$	W*	A	A	A	W		W	W*	W		W	I	W	A	W	W	A	A	A	A	W*	A	W
$\mathrm{Pb''}$	W	A	A	A	(a)	A	W	(a)	(a)	A	(w)	A	A	A	(w)	W*	A	A	A	A	(a)	A	A
$\mathrm{Mg''}$	W	A	A	(w)	W	A	W	W	W	W	W	W	(a)	A	W	W	A	A	A	A	W	A	A
$\mathrm{Mn''}$	W	A	A	A	W	A	W	W	W	A	I	A	A	A	W	W	(w)	A	A	A	W	A	(w)
$\mathrm{Hg''}$	(w)	A	A		(a)	A	W	(a)	A	W			W		A	W*	A	A	A		(w)	A	(w)
$\mathrm{Hg'}$	W	A	A		W	A	W	W	(w)	W	A	A	(w)		A	W*	A	A	A		W	A	A
$\mathrm{Ni''}$	W	A	A	A	W	A	W	W	A	(a)	I	I	(w)	A	W	W*	A	A	A	A	W	A	A
$\mathrm{K'}$	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
$\mathrm{Ag'}$	(w)	A	A	A	I	A	W	I	A	I	I	I	W		I	W	A	A	A		(w)	A	A
$\mathrm{Na'}$	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
$\mathrm{Sn''''}$	W	A			W			W				I	W	A	W	(w)	W	A	A		W	A	
$\mathrm{Sn''}$	W	A	A	A	W		W	W	A		I	I	W	A	W		A	A	A		W	A	A
$\mathrm{Sr''}$	W	A	A	A	W	A	W	W	(w)	W	W	W	(a)	A	W	W	A	(w)	A	A	(a)	W	A
$\mathrm{Zn''}$	W	A		A	W	A	W	W	W	A	A	(a)	(w)	A	W	W	A	A	A	A	W	A	A

Oxides and Hydroxides soluble in a solution of $NaOH$: Pb, As, Sb, Sn, Au, Al, Cr and Zn.

Oxides and Hydroxides soluble in a solution of NH_3 or NH_4 salts are: Ag, Cu, Cd, As, Co, Ni, Mn, Zn and Mg.

*Form a basic salt by interaction with H_2O. A.

TABLE XXII. SOLUBILITIES* OF SALTS AT 18.°

The *upper number* in each square gives the number of grams of the anhydrous salt held in solution by 100 c.c. of water. The *lower number* is the molar solubility, *i. e.*, the number of moles contained in one liter of the saturated solution.

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	0.0_316 0.0_410	0.3 0.013	37.24 1.7	51.09 3.0	73.19 5.4	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	88.76 6.9	168.7 12.6	0.0_41 0.0_66	0.04 0.0_215	103.6 2.9	96.52 3.4	143.3 5.2	103.1 4.6	478.2 9.8	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	0.0_635 0.0_71	0.006 0.0_317	201.4 3.8	169.2 3.9	200 4.8	148.2 4.1	419 6.9	0.08 0.0_22
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	72.05 3	0.16 0.0_292	0.012 0.001	0.0016 0.0_32	0.0076 0.0_214	0.005 0.0_35	0.07 0.003
NO_3	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	8.91 0.35	8.74 0.33	66.27 2.7	121.8 5.2	74.31 4.0	117.8 4.7	51.66 1.4
ClO_3	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	3.69 0.13	35.42 1.1	174.9 4.6	179.3 5.3	126.4 4.7	183.9 5.3	150.6 3.16
BrO_3	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	0.30 0.009	0.8 0.02	30.0 0.9	85.17 2.3	42.86 1.5	58.43 1.8	1.3 0.03
IO_3	7.62 0.35	8.33 0.4	80.43 3.84	0.004 0.0_314	0.059 0.0_216	0.05 0.001	0.25 0.0_257	0.25 0.007	6.87 0.26	0.83 0.02	0.002 0.0_43
OH	142.9 18	116.4 21.	12.04 5.0	0.01 0.001	40.04 1.76	3.7 0.22	0.77 0.063	0.17 0.02	0.001 0.0_32	0.0_35 0.0_45	0.01 0.0_34
SO_4	11.11 0.62	16.83 1.15	35.64 2.8	0.55 0.020	4.74 0.09	0.0_323 0.0_410	0.011 0.0_36	0.20 0.015	35.43 2.8	53.12 3.1	0.0041 0.0_313
CrO_4	63.1 2.7	61.21 3.30	111.6 6.5	0.0025 0.0_315	0.006 0.0_31	0.0_338 0.0_415	0.12 0.006	0.4 0.03	73.0 4.3	. . . . . .	0.0_42 0.0_65
C_2O_4	30.27 1.6	3.34 0.24	7.22 0.69	0.0035 0.0_32	1.48 0.030	0.0086 0.0_338	0.0046 0.0_326	0.0_356 0.0_443	0.03 0.0027	0.0_36 0.0_44	0.0_315 0.0_55
CO_3	108.0 5.9	19.39 1.8	1.3 0.17	0.003 0.0_31	4.95 0.10	0.0023 0.0_311	0.0011 0.047	0.0013 0.0_313	0.1 0.01	0.004? 0.0_33?	0.0_31 0.0_43

*From Smith's General Inorganic Chemistry. Table used by permission of the author.

TABLE XXIII.

Composition of Some of the Important Alloys.

Gold coin (U.S., Fr., Ger.)	Gold	900
	Copper	100
Gold coin (Great Britain)	Gold	916.6
	Copper	83.4
Gold jewelry	Gold	750–920
	Copper	250–80
Silver coin (U. S.)	Silver	900
	Copper	100
Silver coin (Great Britain)	Silver	925
	Copper	75
Silverware (sterling)	Silver	925
	Copper	75
Bronze	Copper	93.5–95
	Tin	6–4
	Zinc	0.5–1
Gun-metal	Copper	100
	Tin	10
Bell-metal	Copper	78
	Tin	22
Speculum-metal	Copper	67
	Tin	33
Aluminum bronze	Copper	90–95
	Aluminum	10–5
Managanese bronze	Copper	90
	Managanese	10
Phosphorus bronze	Copper	90
	Tin	9
	Phosphorus	5–.8
Silicon bronze	Copper	90
	Tin	9
	Silicon	.8
Red brass	Copper	90
	Zinc	10
White brass	Copper	65
	Zinc	35
German silver	Copper	50
	Zinc	25
	Nickel	25
Britannia-metal	Tin	100
	Antimony	8
	Bismuth	1
	Copper	4
Hard pewter	Tin	92
	Lead	8

TABLE XXIII.—Continued.

Soft pewter	Tin	82
	Lead	18
Solder (soft)	Tin (varies)	50
	Lead (varies)	50
Queen's metal	Tin	75
	Antimony	8
	Bismuth	8
	Lead	9
Type-metal	Tin	25
	Lead	50
	Antimony	25
Fusible metal ("Rose's Metal"), fuses at 94° C.	Tin	25
	Lead	25
	Bismuth	50
Fusible metal ("Wood's Alloy"), fuses at 65° C.	Tin	12
	Lead	25
	Bismuth	50
	Cadmium	13
Babbitt metal	Tin	45·5
	Lead	40·
	Antimony	13·
	Copper	1·5

TABLE XXIV.

Scale of Hardness.

Mineralogists have found it convenient to select a number of minerals for the comparison of hardness. They designate the hardness on a scale of 10.

No. 1. Talc. Scratched easily by the finger-nail.
No. 2. Gypsum. Scratched with difficulty by the nail.
No. 3. Calcite. About as hard as a copper coin.
No. 4. Fluorite. Slightly harder than a copper coin.
No. 5. Apatite. Scratched easily by knife-point.
No. 6. Orthoclase. Scratched with difficulty by knife-point.
No. 7. Quartz. Is not scratched by knife-point.
No. 8. Topaz or beryl.
No. 9. Corundum. Similar to "emery."
No. 10. Diamond.

TABLE XXV.

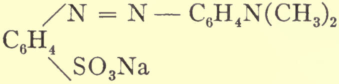
Color Scale of Temperature.

This table is the result of an effort to interpret in terms of thermometric readings, the common expressions used in chemistry in describing temperatures. It is obvious that the values are only approximations.

Color	Temperature.
Incipient red heat.	500°–550°
Dark red heat.	650°–750°
Bright red heat.	850°–950°
Yellowish-red heat.	1050°–1150°
Incipient white heat.	1250°–1350°
White heat.	1450°–1550°

TABLE XXVI.

Indicators.

Phenolphthalein— (A weak acid.)* $C_{20}H_{14}O_4 \rightleftarrows H^{\cdot} + C_{20}H_{13}O'_4$ (Colorless) (red)	Alcohol solution—1 part solid in 100 parts of 60 per cent. alcohol. Colorless by acids; also by CO_2; red by alkalies.
Methylorange— (A weak base.)  $C_6H_4 \begin{cases} N = N - C_6H_4N(CH_3)_2 \\ SO_3Na \end{cases}$	Water solution—1 part solid to 1000 parts of water. Red by mineral acids; not affected by CO_2; yellow color by alkalies.
Litmus—Water solution.	Red by acids; blue by alkalies.
Cochineal—	Alcoholic solution,—3 grm. of powder in 400 parts H_2O and 100 parts alcohol. Yellowish-red by acids; violet by alkalies.

* Stieglitz, Jour. Amer. Chem. Soc. (Nov. 1903).

TABLE XXVII.

Soap-Bubble Solution No. I.

Newth suggests the following formula for preparing soap solutions: "Ten grams of sodium oleate and 400 cm.³ of distilled water are placed in a stoppered bottle, and allowed to stand until the oleate has dissolved, without warming; 100 cm.³ of pure glycerin are then added, and the mixture after being well shaken is allowed to stand in the dark for a few days. The clear solution is then carefully decanted or siphoned into a clean, stoppered bottle, one drop of strong ammonia solution added. If kept in the dark and not exposed to the air, this solution may be preserved for years."

Soap-Bubble Solution No. II.

The following formula will be found to give excellent results: Place about 100 grm. of shavings of the best castile soap in a liter flask; add nearly a liter of distilled water. Shake the mixture until a saturated solution is obtained, then allow it to settle. To two volumes of the clear soap solution add one volume of glyerin. Keep in a stoppered bottle in the dark.

TABLE XXVIII.

Graduated Solutions.

(*a*) *Fehling's Solution.*

This solution is used frequently in making a quantitative determination of sugar. As it decomposes on keeping, it is best kept ("prepared") in the form of two separate solutions: (1) 34.639 grm. of crystallized copper sulphate, made up to 500 cm.^{3} with water; (2) 173 grm. of Rochelle salt and 60 grm. of sodium hydroxide made up to 500 cm.^{3} with water. For use, equal volumes of the two solutions are mixed. 10 cm.^{3} of the deep blue solution thus obtained are completely reduced by 0.05 grm. of dextrose, or by 0.0475 grm. of sucrose, after inversion. The color is discharged during the reduction.

(*b*) *Nessler's Solution.*

This solution is used in estimating ammonia (free). "Dissolve 17 grm. of mercuric chloride (pulverized) in 300 cm.^{3} of water, and 35 grm. of potassium iodide in 100 cm.^{3} of water. Pour the mercuric chloride solution into the potassium iodide until a permanent red precipitate is formed. Add a 20 per cent. solution of sodium hydroxide until the volume of the mixed solution amounts to one liter. Keep this solution in a cool, dark place—portions of the solution to be removed as needed. It is necessary to "sensitize" the solution before it is ready for use; this is accomplished by adding slowly a saturated solution of mercuric chloride, with constant stirring, until a permanent red precipitate forms: Allow the solution to stand until the solids subside, or filter. It is now ready for use and should have a light, straw-yellow color. The solution deteriorates by standing."

TABLE XXIX.

Percentage and Specific Gravity of Solutions at 15° C.

(*a*) *Sulphuric Acid* (*Lunge and Isler*).

Specific Gravity.	Per cent. H_2SO_4.	Specific Gravity.	Per cent. H_2SO_4.	Specific Gravity.	Per cent. H_2SO_4.
1.000	0.00	1.320	41.50	1.640	71.99
1.010	1.57	1.330	42.66	1.650	72.88
1.020	3.03	1.340	43.74	1.660	73.64
1.030	4.49	1.350	44.82	1.670	74.51
1.040	5.96	1.360	45.88	1.680	75.42
1.050	7.37	1.370	46.94	1.690	76.30
1.060	8.77	1.380	48.00	1.700	77.17
1.070	10.19	1.390	49.06	1.710	78.01
1.080	11.60	1.400	50.11	1.720	78.92
1.090	12.99	1.410	51.15	1.730	79.80
1.100	14.35	1.420	52.15	1.740	80.68
1.110	15.71	1.430	53.11	1.750	81.56
1.120	17.01	1.440	54.07	1.760	82.44
1.130	18.31	1.450	55.03	1.770	83.32
1.140	19.61	1.460	55.97	1.780	84.50
1.150	20.91	1.470	56.90	1.790	85.70
1.160	22.19	1.480	57.83	1.800	86.90
1.170	23.47	1.490	58.74	1.810	88.30
1.180	24.76	1.500	59.70	1.820	90.05
1.190	26.04	1.510	60.65	1.825	91.00
1.200	27.32	1.520	61.59	1.830	92.10
1.210	28.58	1.530	62.53	1.834	93.05
1.220	29.84	1.540	63.43	1.837	94.20
1.230	31.11	1.550	64.26	1.839	95.00
1.240	32.28	1.560	65.08	1.840	95.60
1.250	33.40	1.570	65.90	1.841	97.00
1.260	34.57	1.580	66.71	1.8415	98.20
1.270	35.71	1.590	67.59	1.841	98.70
1.280	36.87	1.600	68.51	1.840	99.20
1.290	38.03	1.610	69.43	1.839	99.70
1.300	39.19	1.620	70.32		
1.310	40.35	1.630	71.16		

TABLE XXIX.—Continued.

(*b*) *Hydrochloric Acid.**

Specific Gravity.	Per cent. HCl.	Specific Gravity.	Per cent. HCl.	Specific Gravity.	Per cent. HCl.
1.000	0.16	1.070	14.17	1.140	27.66
1.005	1.15	1.075	15.16	1.145	28.61
1.010	2.14	1.080	16.15	1.150	29.57
1.015	3.12	1.085	17.13	1.155	30.55
1.020	4.13	1.090	18.11	1.160	31.52
1.025	5.15	1.095	19.06	1.165	32.49
1.030	6.15	1.100	20.01	1.170	33.46
1.035	7.15	1.105	20.97	1.175	34.42
1.040	8.16	1.110	21.92	1.180	35.39
1.045	9.16	1.115	22.86	1.185	36.31
1.050	10.17	1.120	23.82	1.190	37.23
1.055	11.18	1.125	24.78	1.195	38.16
1.060	12.19	1.130	25.75	1.120	39.11
1.065	13.19	1.135	26.70		

* Lunge and Marchlewski in Zeit. f. angew. Chem. 1891, 133.

(*c*) *Nitric Acid.* (*Lunge and Rey.*)

Specific Gravity.	Per cent. HNO_3	Specific Gravity.	Per cent. HNO_3	Specific Gravity.	Per cent. HNO_3
1.00	0.00	1.18	29.38	1.36	57.57
1.01	1.90	1.19	30.88	1.37	59.39
1.02	3.70	1.20	32.36	1.38	61.27
1.03	5.50	1.21	33.82	1.39	63.23
1.04	7.26	1.22	35.28	1.40	65.30
1.05	8.99	1.23	36.78	1.41	67.50
1.06	10.68	1.24	38.29	1.42	69.80
1.07	12.33	1.25	39.82	1.43	72.17
1.08	13.95	1.26	41.34	1.44	74.68
1.09	15.53	1.27	42.87	1.45	77.28
1.10	17.11	1.28	44.41	1.46	79.98
1.11	18.67	1.29	45.95	1.47	82.90
1.12	20.23	1.30	47.49	1.48	86.05
1.13	21.77	1.31	49.07	1.49	89.60
1.14	23.31	1.32	50.71	1.50	94.09
1.15	24.84	1.33	52.37	1.51	98.10
1.16	26.36	1.34	54.07	1.52	99.67
1.17	27.88	1.35	55.79		

TABLE XXIX.—Continued.

(*d*) *Ammonium Hydroxide.**

Specific Gravity.	Per cent. NH_4.	Specific Gravity.	Per cent. NH_3.	Specific Gravity.	Per cent. NH_3.
0.882	34.95	0.922	21.12	0.962	9.35
0.884	34.10	0.924	20.49	0.964	8.84
0.886	33.25	0.926	19.87	0.966	8.33
0.888	32.50	0.928	19.25	0.968	7.82
0.890	31.75	0.930	18.64	0.970	7.31
0.892	31.05	0.932	18.03	0.972	6.80
0.894	30.37	0.934	17.42	0.974	6.30
0.896	29.69	0.936	16.82	0.976	5.80
0.898	29.01	0.938	16.22	0.978	5.30
0.900	28.33	0.940	15.63	0.780	4.80
0.902	27.65	0.942	15.04	0.982	4.30
0.904	26.98	0.944	14.46	0.984	3.80
0.906	26.31	0.946	13.88	0.986	3.30
0.908	25.65	0.948	13.31	0.988	2.80
0.910	24.99	0.950	12.74	0.990	2.31
0.912	24.33	0.952	12.17	0.992	1.84
0.914	23.68	0.954	11.60	0.994	1.37
0.916	23.03	0.956	11.03	0.996	0.91
0.918	22.39	0.958	10.47	0.998	0.45
0.920	21.75	0.960	9.91	1.000	0.00

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* Lunge and Wiernick in Ziet. f. angew. Chem. 1889, 183.

TABLE XXX.

Proportion by Weight of Absolute Alcohol.
*(Mendeléef.)**

Specific gravity at 15° C.	Per cent. of alcohol.	Specific gravity at 15° C.	Per cent of alcohol.	Specific gravity at 15° C.	Per cent. of alcohol.
0.9991	0.5	0.9501	34	0.8773	68
0.9981	1	0.9491	35	0.8750	69
0.9963	2	0.9473	36	0.8726	70
0.9945	3	0.9455	37	0.8702	71
0.9928	4	0.9436	38	0.8678	72
0.9912	5	0.9417	39	0.8655	73
0.9896	6	0.9397	40	0.8631	74
0.9881	7	0.9377	41	0.8607	75
0.9867	8	0.9357	42	0.8582	76
0.9853	9	0.9336	43	0.8558	77
0.9839	10	0.9316	44	0.8534	78
0.9826	11	0.9294	45	0.8510	79
0.9813	12	0.9273	46	0.8485	80
0.9801	13	0.9251	47	0.8460	81
0.9789	14	0.9230	48	0.8435	82
0.9777	15	0.9208	49	0.8410	83
0.9765	16	0.9186	50	0.8386	84
0.9753	17	0.9164	51	0.8360	85
0.9741	18	0.9142	52	0.8335	86
0.9728	19	0.9119	53	0.8309	87
0.9716	20	0.9097	54	0.8283	88
0.9704	21	0.9074	55	0.8257	89
0.9691	22	0.9052	56	0.8230	90
0.9678	23	0.9029	57	0.8203	91
0.9665	24	0.9097	58	0.8176	92
0.9651	25	0.8983	59	0.8149	93
0.9637	26	0.8960	60	0.8120	94
0.9623	27	0.8937	61	0.8092	95
0.9608	28	0.8914	62	0.8063	96
0.9593	29	0.8890	63	0.8034	97
0.9577	30	0.8867	64	0.8004	98
0.9561	31	0.8844	65	0.7973	99
0.9544	32	0.8820	66	0.7942	100
0.9527	33	0.8797	67		

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*Pogg. Ann. 138, p. 103.

TABLE XXXI.

Proportion by Volume of Absolute Alcohol.
(*Mendeléef.*)*

100 volumes spirits.		100 volumes spirits.		100 volumes spirits.	
Specific gravity at 15.5° C.	Contain volumes of alcohol.	Specific gravity at 15.5° C.	Contain volumes ot alcohol	Specific gravity 15.5° C.	Contain volumes of alcohol.
1.0000	0	0.9604	34	0.8950	68
0.9985	1	0.9591	35	0.8925	69
0.9970	2	0.9577	36	0.8901	70
0.9956	3	0.9563	37	0.8876	71
0.9942	4	0.9548	38	0.8851	72
0.9928	5	0.9534	39	0.8825	73
0.9915	6	0.9518	40	0.8800	74
0.9902	7	0.9503	41	0.8774	75
0.9889	8	0.9486	42	0.8747	76
0.9877	9	0.9470	43	0.8721	77
0.9866	10	0.9454	44	0.8694	78
0.9854	11	0.9436	45	0.8667	79
0.9844	12	0.9419	46	0.8640	80
0.9832	13	0.9400	47	0.8611	81
0.9822	14	0.9382	48	0.8583	82
0.9811	15	0.9364	49	0.8554	83
0.9801	16	0.9344	50	0.8525	84
0.9790	17	0.9325	51	0.8496	85
0.9781	18	0.9305	52	0.8466	86
0.9771	19	0.9285	53	0.8435	87
0.9761	20	0.9265	54	0.8404	88
0.9751	21	0.9244	55	0.8372	89
0.9741	22	0.9222	56	0.8340	90
0.9731	23	0.9201	57	0.8306	91
0.9720	24	0.9180	58	0.8272	92
0.9709	25	0.9158	59	0.8236	93
0.9699	26	0.9139	60	0.8199	94
0.9688	27	0.9113	61	0.8161	95
0.9677	28	0.9090	62	0.8121	96
0.9667	29	0.9067	63	0.8080	97
0.9654	30	0.9045	64	0.8035	98
0.9642	31	0.9022	65	0.7989	99
0.9630	32	0.8997	66	0.7939	100
0.9617	33	0.8974	67		

*Pogg. Ann., 138, 230.

TABLE XXXII. LIST OF ELEMENTS.

(International Atomic Weights, 1908.)

The following list of atomic weights is taken from the report of the "International Committee on Atomic Weights." (*Jour. Am. Chem. Soc.*, Jan. 1908.)

NAME.	SYMBOL.	VALENCES.	AT. WT.	DISCOVERED OR ISOLATED BY.	DATE.
Aluminum	Al.	III	27.1	Wöhler	1827
Antimony (Stibium)	Sb.	III–IV	120.2	Basil Valentine	15th Cent.
Argon	A.	O	39.9	Rayleigh and Ramsay	1894
Arsenic	As.	III–V	75.0	Albertus Magnus or Schroder	13th or 17th Cent.
Barium	Ba.	II	137.4	Davy	1808
Bismuth	Bi.	III	208.0	Basil Valentine	15th Cent.
Boron	B.	III	11.0	Gay-Lussac and Thenard	1808
Bromine	Br.	I–V	79.96	Balard	1826
Cadmium	Cd.	II	112.4	Stromeyer	1817
Caesium	Cs.	I	132.9	Bunsen and Kirchoff	1860
Calcium	Ca.	II	40.1	Davy	1808
Carbon	C.	IV–II	12.00		Ancient
Cerium	Ce.	IV–III	140.25	Mosander	1839
Chlorine	Cl.	I–V–VII–III	35.45	Scheele	1774
Chromium	Cr.	III–VI–VII–II	52.1	Vauquelin	1797
Cobalt	Co.	II–III	59.0	Brandt	1735
Columbium (Niobium)	Cb.	V–III	94.	Hatchett	1801
Copper (Cuprium)	Cu.	II–I	63.6		Ancient.
Dysprosium	Dy.	III (?)	162.5	Urbain and Demenitroux	1907
Erbium	Er.	III	166.	Mosander	1843
Europium	Eu.	?	152.	Demarcay	1901
Fluorine	F.	I	19.0	Moissan	1886
Gadolinium	Gd.	III	156.		
Gallium	Ga.	III	70.0	Lecoq de Boisbaudran	1875

TABLE XXXII.—CONTINUED.

NAME.	SYMBOL.	VALENCES.	AT. WT.	DISCOVERED OR ISOLATED BY.	DATE.
Germanium	Ge.	IV–II	72.5	Winkler	1886
Glucinum (Beryllium)	Gl.	II	9.1	Wohler and Bussy	1828
Gold (Aurum)	Au.	I–III	197.2		Ancient.
Helium	He.	O	4.0	Ramsay and Cleve	1895
Hydrogen	H.	I	1.008	Cavendish	1766
Indium	In.	III	115.0	Reich and Richter	1863
Iodine	I.	I–V–VII	126.97	Courtois	1811
Iridium	Ir.	III–IV–II	193.0	Smithson Tennant	1804
Iron (Ferrum)	Fe.	III–II	55.9		Ancient.
Krypton	Kr.	O	81.8	Ramsay and Travers	1898
Lanthanum	La.	III	138.9	Mosander	1839
Lead	Pb.	II–IV	206.9		Ancient.
Lithium	Li.	I	7.03	Arfvedson	1817
Magnesium	Mg.	II	24.36	Liebig and Bussy	1830
Manganese	Mn.	II–IV–VII–VI–III	55.0	Gahn	1774
Mercury (Hydrargyrum)	Hg.	II–I	200.0		Ancient.
Molybdenum	Mo.	VI–IV–II	96.0	Hjelm	1790
Neodymium	Nd.	III	143.6	Auer von Welsbach	1885
Neon	Ne.	O	20.	Ramsay and Travers	1898
Nickel	Ni.	II–III	58.7	Cronstedt	1751
Nitrogen	N.	II–V	14.01	Rutherford	1772
Osmium	Os.	IV–VIII	191.0	Smithson Tennant	1804
Oxygen	O.	II	16.00	Priestly	1774
Palladium	Pd.	IV–II	106.5	Wollaston	1803
Phosphorus	P.	V–III	31.0	Brand	1674
Platinum	Pt.	IV–II	194.8	Watson (?)	1750
Potassium (Kalium)	K.	I	39.15	Davy	1807

TABLE XXXII.—CONTINUED.

NAME.	SYMBOL.	VALENCES.	AT. WT.	DISCOVERED OR ISOLATED BY.	DATE.
Praseodymium	Pr.	III	140.5	Auer von Welsbach	1885
Radium	Ra.	II	225.*	Curie	1902
Rhodium	Rh.	III	103.0	Wollaston	1803
Rubidium	Rb.	I	85.5	Bunsen and Kirchhoff	1861
Ruthenium	Ru.	III–IV–VI–VIII	101.7	Claus	1845
Samarium	Sa.	III	150.3	Lecoq de Boisbaudran	1879
Scandium	Sc.	III	44.1	Nilson and Cleve	1879
Selenium	Se.	II–VI–IV	79.2	Berzelius	1817
Silicon	Si.	IV	28.4	Berzelius	1822
Silver (Argentum)	Ag.	I	107.93		Ancient.
Sodium (Natrium)	Na.	I	23.05	Davy	1807
Strontium	Sr.	II	87.6	Davy	1808
Sulphur	S.	II–IV–VI	32.06		Ancient.
Tantalum	Ta.	V	181.	Ekeberg	1802
Tellurium	Te.	II–IV–VI	127.6	Reichenstein	1782
Terbium	Tb.	III	159.2	Mosander	1843
Thallium	Tl.	I–III	204.1	Crookes	1861
Thorium	Th.	IV–III	232.5	Berzelius	1828
Thulium	Tm.	III	171.	Cleve	1879
Tin	Sn.	II–IV	119.0		Ancient.
Titanium	Ti.	IV	48.1	Gregor	1789
Tungsten (Wolfram)	W.	II–IV–VI	184.0	J. and F. d'Elhujar	1783
Uranium	U.	IV–VI	238.5	Peligot	1841
Vanadium	V.	V–III	51.2	Berzelius (or Wöhler)	1831
Xenon	Xe.	O	128.	Ramsay and Travers	1898
Ytterbium	Yb.	III	173.0	Marignac	1878
Yttrium	Y.	III	89.0	Wöhler	1828
Zinc	Zn.	II	65.4	Probably by Paracelsus	16th Cent.
Zirconium	Zr.	IV	90.6	Berzelius (Klaproth, 1789)	1825

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*Later determinations by Madame Curie: Ra. 226.45.

† See "Elements Verified and Unverified"—Baskerville, in Proceed. of A. A. A. S.—1904.

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INDEX.

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