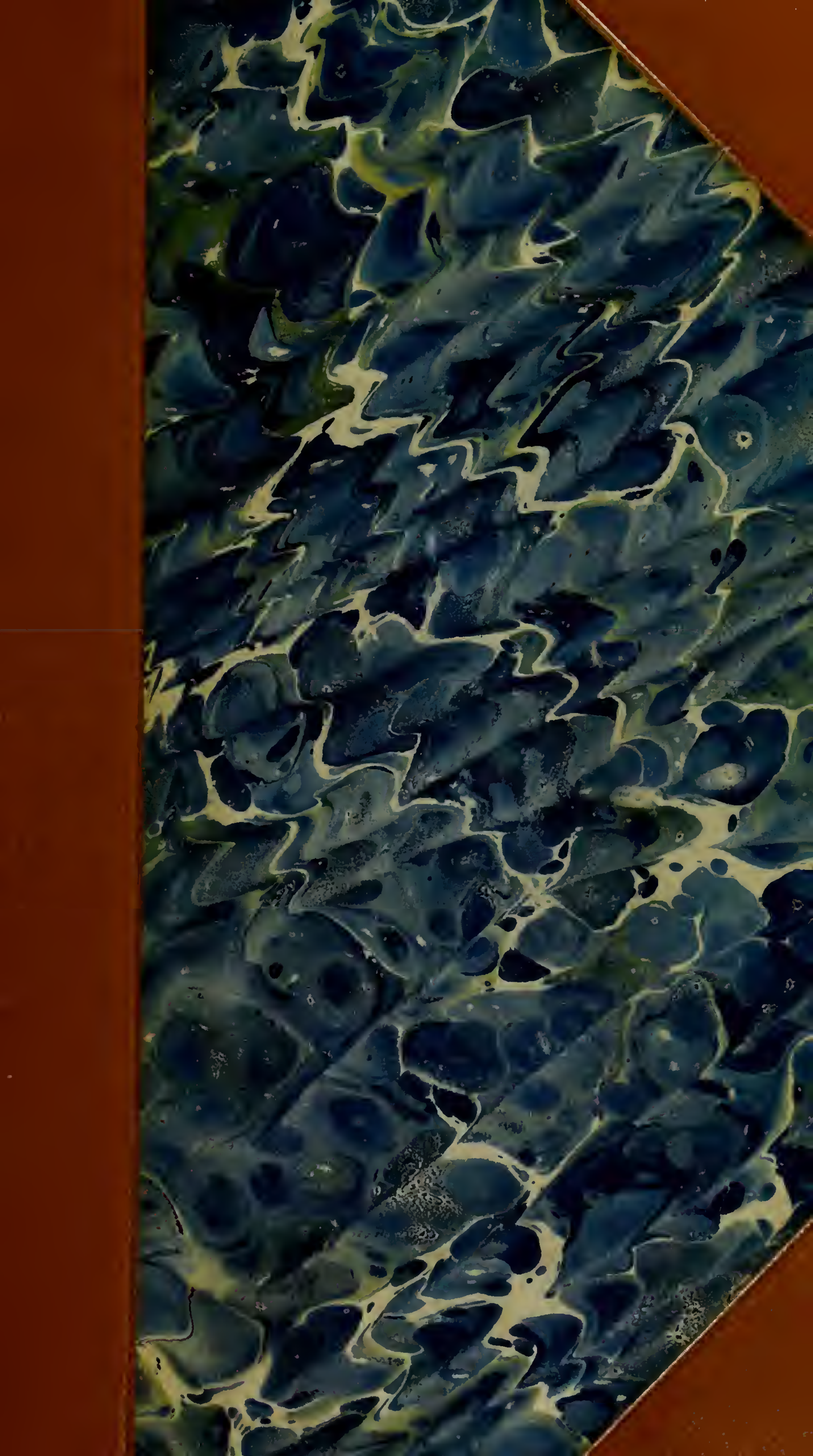


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SYSTEM

OF

CHEMISTRY.

IN FOUR VOLUMES.

BY

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SYSTEM

OF

CHEMISTRY.

BOOK V.

OF EARTHS AND THEIR BASES.

THE EARTHS form the transition from the Fixed Alkalis to the Metallic Oxides. They are less soluble than the former in water, and in general display less activity as chemical agents, while in both these respects they are superior to the latter: they constitute therefore an intermediate order. They are also of similar chemical constitution, being composed of metallic bases with oxygen; and these bases are still more analogous than those of the Fixed Alkalis to the common Metals. The whole form one series, by the characteristic property common to all of them, of neutralizing acidity.

In common language the term Earth is applied to any substance of a loose texture, moderate specific gravity, opaque, dull and insipid, uninflammable, infusible, and of sparing solubility in water. In mineralogy it is understood nearly in the same sense. In chemical language it has a more appropriate signification, being applied to a few bodies, homogeneous, and distinguished by characteristic chemical properties, which, by their mutual combinations, or mixtures, form those substances classed in popular language as earths or stones. It is by analysing these that chemists have arrived at the knowledge of the earths; some of them also exist in saline combinations in the mineral kingdom, and likewise enter into the composition of vegetable and animal matter.

Four earths were known to the older chemists, silex, alumina, magnesia, and lime. Barytes and strontites were afterwards discovered; and within these few years zircon, glucine, and ittria, have been made known: still more recently another earth, thorina, has been added to the number. These last exist in nature in very sparing quantity; and the first four are the principal constituents of earthy minerals.

The earths having, in many of their properties, a strict analogy with metallic oxides, were often supposed to be metals saturated with oxygen, and attempts were made to reduce them to the metallic state. These at one time appeared to be successful; metallic grains having been obtained in a series of experiments by Tondi and Ruprecht, by exposing to intense heat, barytes, lime, and magnesia, in mixture with charcoal, covered with powder of calcined bone *. Klaproth and Savaresi, however, proved that these metallic grains are phosphuret of iron, derived from the charcoal, the matter of the crucible, and the calcined bones †. At a later period Desormes and Guyton inferred, that the earths are compounds, containing hydrogen and nitrogen ‡; but Darracq shewed, that the results whence

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* Crell's Chemical Journal, vol. i.

† Annales de Chimie, tom. x. p. 254. 275.

‡ Mémoires de l'Institut. National, tom. iii.

this conclusion was drawn, had arisen from impurities in the substances operated on *.

After the decomposition of the fixed alkalis had been effected by galvanism, Mr Davy submitted the earths to the same powerful instrument of analysis. The results, however, were much less distinct; the earths are non-conductors of electricity, and being infusible, and not easily acted on by water, they could not be rendered conductors by the same methods as those which had succeeded with the alkalis: slight changes therefore only were produced. By adding in the experiment potash, or certain metallic oxides, the results were less ambiguous, alloys being obtained, which contained matter derived from the decomposition of the earths. But a method employed by Berzelius and Pontin succeeded better. It consisted in placing at the negative side of a galvanic battery, quicksilver in contact with the earths, and completing the circuit: they thus decomposed barytes and lime, and obtained their bases in combination with the quicksilver. Mr Davy, by following this method, decomposed strontites and magnesia; and succeeded to a certain extent in separating the quicksilver by distillation. Silex, alumina, zircon, and glucine, appeared to suffer little change; but in submitting them to the action of galvanism, combined with potash and soda in fusion, appearances were obtained which indicated their decomposition, and the production of bases of a metallic nature †.

In later experiments, attempts were made to decompose the earths, by submitting them to the action of potassium, at a high temperature, either alone or with quicksilver or iron-filings; and by the latter arrangement, more distinct results were obtained: from the mixtures containing silica,

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* Philosophical Magazine, vol. xi. p. 541.

† Philosophical Transactions, 1808.

alumina, or glucine, masses were obtained, having metallic characters, and which, on being dissolved in acids, afforded by treatment with re-agents, oxide of iron, alkali, and sensible quantities of the earth employed in the experiment: from the alkaline earths, solid amalgams, containing the metallic matter of the earth employed, were also procured *.

Gay Lussac and Thenard also, submitting the earths in contact with quicksilver to the action of a very powerful galvanic battery, obtained from barytes, strontites, and lime, amalgams which produced effervescence in water and rendered it alkaline †.

From all these experiments, it is established, that the alkaline earths are of chemical constitution, analogous to that of the fixed alkalis; and there is every probability, that this is true with regard to the others. They are compounds of metallic bases with oxygen; and as the earths themselves approach more nearly to the common metallic oxides in their properties, so their bases are more analogous to the common metals, having greater hardness and specific gravity than the alkaline metalloids. Some of the earths have been stated to be reduced to the metallic state by the intense heat excited by the mixture of oxygen and hydrogen, but the results with regard to this are doubtful. The base of siliceous earth has not been obtained altogether insulated, and from some appearances it has been inferred to be rather analogous to the simple inflammables, than to a metal.

Though the Earths are connected by their properties and chemical relations with the alkalis on the one hand, and with the metallic oxides on the other, there are sufficient grounds for considering them as a separate order. Under this point of view, the distinctive characters which

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* Philosophical Transactions, 1810.

† Recherches Physico-Chimiques, tom. i. p. 50. 106.

belong to them, as well as certain general properties they possess, require to be pointed out, before proceeding to their individual history.

Of these properties, the absence of inflammability is characteristic: this arises from their being substances saturated with oxygen. Though uninflammable, it was affirmed by Humboldt, and by some other chemists, that several of the earths absorb oxygen when exposed in a humid state to atmospheric air*. But it was demonstrated by Saussure *junior*, Chaptal, and others, that there is no such absorption by the pure earths, nor any affinity exerted by them to oxygen †. Gay Lussac and Thenard, however, have found, that ignited barytes absorbs oxygen at a high temperature, passing to a higher state of oxidation, a property rendering more complete its analogy to the fixed alkalis.

Infusibility is a more appropriate character of the earths, and in particular distinguishes them from the alkalis. They are of very difficult fusibility; nearly all of them requiring an intense heat for their fusion, and some of them resisting the strongest heat that has been applied; silica and alumina remain unmelted in the heat of the most powerful burning mirror, and lime and magnesia are not fully melted in the more intense heat excited by the stream of oxygen gas directed on burning charcoal. They have been fused, however, in the flame of the condensed mixture of oxygen and hydrogen gases. When mixed with each other they are more fusible; the one promoting the fusion of the other by the mutual affinities they exert, and the formation of a fusible compound.

They are in general sparingly soluble in water. Magnesia, alumina, and silica, are not dissolved in any appreciable quantity. Lime dissolves in 700 times its weight

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* Journal de Physique, tom. xlviii. p. 132.

† Nicholson's Journal, 4to, vol. iv. p. 373.

of water, strontites in less than in 200, and barytes in 25 parts. These three earths, when in a dry state, attract water in considerable quantity, and enter into intimate combination with it, by which their cohesion is destroyed, and they are reduced to powder. The others imbibe water in their precipitation from any state of solution, and retain it under a considerable degree of heat. Magnesia, alumina, and silica, exist also in nature in combination with definite proportions of water. The same view, however, may be applied to the Hydrates of the Earths, as that which I have applied to the alkaline hydrates: they may be ternary compounds of the metallic base with oxygen and hydrogen; the water which they absorb when added to them in what is called their dry state, may be resolved into these elements, which may pass into this state of combination; and the water they yield may be formed in the processes by which it is obtained. If this view be adopted, the principal difference which the earths exhibit compared with the alkalis, is that of being more easily obtained as oxides, free from the portions of oxygen and hydrogen which constitute what has been considered as their combined water.

The earths combine with the acids, and the greater number of them neutralize the acid properties. One of them, silica, unites with only a few of the acids, principally with the fluoric, and in small quantity with the phosphoric, boracic, and muriatic; and with these, even scarcely produces the state of neutralization. But with regard to the others, there is no such limitation. The compounds of the acids with the earths are similar, in their general properties, to the compounds of the acids with the alkalis. Many of them are soluble and crystallizable; others are of sparing solubility; and all are neutral, when the due proportion of earth and acid is observed. The affinities of some of these earths, particularly of barytes and strontites, to the acids, have been supposed superior to the affinities of the alkalis to the acids, as they decompose a number of the salts which the alkalis form. But, according to the doctrine of Berthollet, which has been fully illustrated in considering the laws of chemical attraction, this is owing to the insolubility of the compounds of those earths with the acids, the salts of which they decompose; the force of cohesion exerted relative to the solvent, and not the superior affinity, determining the decomposition.

The same view must be applied to the compounds formed from the action of the acids on the earths, as to those formed from the action of the acids on the alkalis; and which has been sufficiently illustrated in the consideration of this subject under the theory of acidity.

One chemical character has been assigned to the earths in their combinations with the acids, and particularly distinguishing them from the metals,—that their solutions are not precipitated by prussic acid, or the prussiates. To this, however, there are exceptions, in ittria, and, according to Klaproth, in zircon; these earths affording precipitates with prussiate of potash. The not being precipitated by infusion of galls, is another test by which the earths are distinguished from the metallic oxides, but the two earths now mentioned, also glucine, afford exceptions to it. Neither are the earthy salts in general precipitated by the hydrosulphurets, which affords another character to distinguish them from metallic oxides; though it is not without exceptions. Their salts are not coloured. An exception to this last property has been supposed to exist in the salts of ittria, several of these having a red colour; but this arises from adhering metallic matter.

The alkaline earths combine with the primary inflammables, sulphur and phosphorus, in the same manner as the alkalis do, and with similar results, particularly in the relation of the compounds thus formed to water, which they decompose in the same manner.

The earths and alkalis have mutual affinities. By fusion, the fixed alkalis combine with them, and form vitrifiable compounds. And, in the humid way, potash and soda dissolve alumina, glucine, and silica. Liquid ammonia dissolves a small portion of alumina, and perhaps of lime.

The earths and the metallic oxides are capable of combining with each other; and some of the oxides, those of lead for example, promote greatly the fusion of the earths. By these combinations, coloured glasses are generally formed. The affinities of the earths and metallic oxides are even exerted in the humid way. The effect of oxide of iron in promoting the consolidation of earthy particles, in a soft or humid state, has been long known; lime can even render soluble in water the oxides of mercury, of lead, and some other metals; and barytes and strontites, in decomposing some of the metallic salts, if added in excess, re-dissolve the oxide, which at the first addition they precipitate.

The earths have also affinities to each other. By fusion, many of them combine, forming vitreous compounds, transparent or opaque; and in consequence of their mutual affinities, two earths mixed together generally melt at a heat inferior to that which would be necessary to fuse either of them. Some facts had also been observed, which proved the exertion of affinities between the earths in the humid way; such as the gradual induration of various earthy mixtures, particularly of lime and silex from a humid state. Scheele observed, that in precipitating alumina from its solutions by lime, if an excess be added, the precipitate is re-dissolved, and forms a gelatinous substance; and Vauquelin found, that alumina is capable of combining with barytes and strontites, when it is boiled with them in water. This was made the subject of a series of experiments by Guyton *; and although some of the results he obtained

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* Nicholson's Journal, 4to, vol. iii. p. 419.

appear, from the subsequent researches of Darracq [*], to have arisen from the impurity of the substances on which he operated, a number of important facts, confirmed by Darracq's experiments, with regard to the mutual affinities of the earths in the humid way, and the changes produced in the affinities they exert to other substances, were established. Thus, if the solution of silica in potash, and the solution of alumina in the same alkali, be mixed together, a copious gelatinous precipitate is soon formed, consisting of the two earths in combination; and, what is singular, though the silex alone is scarcely soluble in any of the acids, it is by this combination with alumina rendered soluble in the weakest of them, as for example in distilled vinegar. Lime-water mixed with a solution of silica in liquid potash, forms a precipitate from the union of the two earths; and a similar effect results from adding to the same solution of silica, a solution of barytes, or of strontites in water. When the earths are dissolved in acids, the affinities exerted by the acids to them seem to be too powerful to admit of the mutual affinities of the earths bringing them into combination, so as to separate them from the solvent; for although some separations of this kind appeared to be established by Guyton's experiments, they were not found to take place by Darracq, when the solutions were pure. These effects require to be attended to in mineral analysis. The principal facts with regard to them will be found under the history of each earth.

Several of the earths have the characteristic properties of the alkalis. They are soluble in water; have much acrimony; change the vegetable colours to a green; combine with oils; precipitate metallic oxides from their solutions, and exert strong attractions to the acids. These properties are conspicuous in barytes, strontites, and lime; hence they have been named Alkaline Earths, and Fourcroy even

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[*] Philosophical Magazine, vol. xi. p. 341.

arranged barytes and strontites with the alkalis. It has already been remarked, that the alkalis and earths form a series, in which there is a gradation from the two extreme substances, ammonia and silica, so that, wherever the division into two orders is established, the substances commencing each will have common properties. Of the properties above enumerated, the greater number are not peculiar to the alkalis and to these two earths, but are also possessed by lime, magnesia, alumina, and even by some of the metallic oxides. The connection of barytes and strontites is on the whole more complete with lime, which is on the other side connected with magnesia, than it is with the alkalis; and their more sparing solubility in water, their insolubility in alkohol, their greater infusibility, and their relations to the acids, particularly in forming with the great number of them insoluble salts, rather determine their classification among the earths. They form, however, the transition from the one order to the other, and their history is therefore first to be delivered. Ittria forms the link which connects the earths with the common metals. Silica is equally remote from the alkalis and metallic oxides, and has little analogy to any other substance.

CHAP. I.

OF BARYTES AND ITS BASE.

We are indebted to Gahn and Scheele for the discovery of this earth. Scheele observed it in the course of his experiments on grey ore of manganese, in some varieties of which it appears to exist; and Gahn proved, that in the fossil which had been known to mineralogists under the name of Heavy Spar, it exists in combination with sulphuric acid. From the great weight of the mineral from which it is obtained, as well as of the earth itself, it was named Terra Ponderosa,—a name changed by Guyton and Kirwan to Barytes; and which, to obtain analogy of termination, has been farther changed into Baryta.

Barytes forms a component part of few fossils: it occurs almost exclusively in combination with sulphuric acid, or with carbonic acid. From either of these it may be procured.

It may be obtained from the native carbonate, by exposure to the heat of a forge in a black-lead crucible, as Dr Hope pointed out *. A little charcoal added facilitates the expulsion of the carbonic acid, by converting it into carbonic oxide. By lixiviating the residual matter with boiling water, the barytes is dissolved, and may be crystallized.

To obtain barytes from the native sulphate, any quantity of the latter reduced to powder is mixed with one-third its weight of charcoal, and exposed in a covered crucible to a

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* Edinburgh Philosophical Transactions, vol. iv. p. 34.

red heat for two hours. The sulphuric acid of the sulphate is decomposed, its oxygen being attracted by the charcoal; the sulphur remains combined with the barytes. Water is poured on the residuum when cold, and boiled on it for a short time: the sulphuret of barytes is dissolved, and re-acting on the water, causes a formation of sulphuretted hydrogen, which uniting with the barytes, a hydro-sulphuret, or sulphuretted hydro-sulphuret of barytes, remains in solution. The barytes may be precipitated in the state of carbonate, by the addition of carbonate of soda, and this, when dry, may be decomposed in the same way as the native carbonate. Or, according to a process given by Vauquelin, diluted nitric acid may be added to the liquor obtained by washing the sulphuret of barytes in water, continuing the addition as long as there is any precipitation of sulphur, or disengagement of sulphuretted hydrogen: the solution is filtered, and the nitrate of barytes crystallized by evaporation; it is then decomposed by exposure to a red heat in a platina crucible *. The nitrate for this purpose may also be formed by dissolving the native carbonate in diluted nitric acid.

Besides the analogy between the earths and metallic oxides, barytes seemed to have some properties denoting it more peculiarly to be of a metallic nature; such were the great specific gravity of some of its saline combinations, and its poisonous quality. The attempts, however, to reduce it to the metallic form were equally unsuccessful with those on other earths.

Sir H. Davy obtained indistinct appearances of metallization, by the usual method of submitting it to galvanic action; but the complete reduction was best obtained, in the mode of experiment performed by Berzelius and Pontin, placing it in contact with quicksilver, at the negative side of the galvanic battery. On repeating this expe-

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* Nicholson's Journal, 4to, vol. i. p. 555.

riment, the mercury became less fluid;—on exposing the amalgam to the air, it was covered with a film of barytes; and when thrown into water, hydrogen was disengaged, and barytes formed. The reduction was still better obtained, when the earth slightly moistened, and mixed with one-third of red oxide of mercury, was placed on a plate of platina; the whole covered by a film of naphtha, and the plate made positive, the mercury negative, by communication with a powerful battery. An amalgam was obtained; and by applying heat to this, with due precautions to exclude the air, the quicksilver was volatilized. It was very difficult, however, to obtain a complete decomposition, a red heat being required for this, and at this heat the base of the earth acted on the glass: there remained, therefore, the uncertainty but that the metallic base procured retained in combination a little quicksilver. Gay Lussac and Thenard endeavoured to decompose barytes by the action of iron, at a high temperature, in the method by which they had effected the decomposition of potash, but without success; and even in submitting it to the action of potassium at a high temperature, no distinct result indicating decomposition was obtained *.

To the metallic matter obtained from barytes, by the method above described, Davy gave the name of Barium. It appeared as a metal of a grey colour. It was fixed at all common temperatures, but became fluid at a heat below

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* The reduction of barytes to the metallic state has been stated by Dr Clarke to be effected by exposing the earth mixed with oil to the kindled stream of hydrogen and oxygen gases, a film with metallic lustre, of a white colour, appearing on the surface of the exposed mass. But some obscurity exists with regard to this: the results have not been uniform or altogether unequivocal, and the experiment has not succeeded with other chemists. (Annals of Philosophy, vols. viii. ix. x. xi. Journals of the Royal Institution, vol. iii.).

redness, and did not rise in vapour when heated to redness in a tube of glass. It acted, however, violently on the glass, producing a black mass, which seemed to contain barytes and an alkaline base in the first degree of oxygenation. When exposed to air, it rapidly tarnished, and fell into a white powder, which was barytes; and when this process was conducted in a small portion of air, oxygen was absorbed. When dropt into water, it sunk to the bottom, producing barytes, and generating hydrogen gas. It not only sunk in water, but even in sulphuric acid, though surrounded by globules of gas; hence it was concluded that it cannot be less than four or five times heavier than water. It flattened by pressure, but required for this purpose a considerable force.

Davy was unable to determine the proportion of base and oxygen in the composition of barytes; he ascertained only that the metal burned in a small quantity of air, absorbed oxygen, gained weight in the process, and that the earth produced was in the driest state. Its composition, however, can be indirectly inferred from the principle pointed out by Berzelius, as following from the law of Gay Lussac with regard to the relation of acids to metallic oxides,—that the quantity of acid combined with the oxide is proportional to the quantity of oxygen combined with the metal; and hence the latter may be inferred from the former, a given weight of an acid always saturating a quantity of base containing a certain quantity of oxygen: 100 parts for example, of what is called real sulphuric acid, saturate a quantity of base containing 20 of oxygen. It is necessary, therefore, only to determine what quantity of barytes is saturated by 100 of sulphuric acid; this gives the quantity of oxygen, and of course the proportion of barium. The quantity is 194 parts, and reducing the proportions to 100, this gives as the composition of barytes 89.6 of barium, and 10.4 of oxygen.

Gay Lussac and Thenard found, that barytes is not the oxide at the maximum, but that it absorbs oxygen when exposed to the air at a moderate heat. It even has this property in a more remarkable degree than the fixed alkalis. When heated in a glass tube in pure oxygen gas, the oxygen is absorbed with rapidity; and the barytes becomes vitrified at the surface, and of a greyish colour. In this state it yields oxygen to inflammable bodies; water also disengages oxygen from it, as does a sudden intense heat; when heated in hydrogen gas, it absorbs it rapidly, emitting ignited sparks, and the water formed is retained by the barytes *. It appears, therefore, that this substance is the oxide at the maximum of oxidation, and these facts confirm the analogy between barytes and the alkalis. It is necessary that the barytes should be as free from water as possible, to obtain this absorption of oxygen.

Barytes, in the state in which it is obtained by the decomposition of its nitrate by heat, is in the form of a grey, solid, and porous mass. Its specific gravity is about 4. Its taste is harsh and caustic, even more so than that of lime; and it destroys the texture of animal matter. It is the only earth which is poisonous to animals. From exposure to the air, it splits, falls to pieces, and at length passes to the state of a white powder, in consequence of the absorption of water,—an operation analogous to the slaking of lime. It thus increases in weight, according to Vauquelin, to the extent of 0.22, from the absorption of water and carbonic acid. When water is poured on its fragments, they absorb it rapidly, split with a hissing noise, much heat is produced, and they fall into a bulky white powder. If much water is present, it boils, and dissolves a large portion of the barytes, which, as the solution cools, crystallizes in transparent prisms, and if there is not an excess of water, these consolidate, and at length form a hard mass.

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* Recherches Physico-Chimiques, tom. i. p. 170.

The fusibility of barytes has been variously estimated. In its crystallized state, it melts from a very moderate heat; and after it ceases to exhale watery vapour, it flows smoothly at a bright red heat: this on cooling forms a semi-transparent glass, which is again fusible: it contains, however, a considerable portion of water, to which this fusibility is owing. It has been observed, that in the dry porous state in which it is obtained by the decomposition of the nitrate, it is much less fusible; and some have affirmed that it is infusible. It appears, however, that it can be melted by an intense heat; the degree of which has been estimated variously, as more or less water has remained in the barytes according to the manner of effecting the decomposition of the nitrate. Vauquelin states, that when heated before the blow-pipe on charcoal, it forms an opaque globule. Fourcroy observed, that if it be gradually heated, it rather hardens, probably from a progressive expulsion of water. Lavoisier found it to be infusible in the heat excited by oxygen gas directed on burning charcoal *. Guyton, however, succeeded in melting it by this heat †. Mr Hare found it likewise to melt, exposed, either on a support of charcoal or of silver, to the kindled flame of oxygen and hydrogen gases ‡. Davy observed, that the barytes formed from the oxygenation of its base is not fusible at an intense heat.

Barytes, thoroughly dried by exposure to a red heat, was supposed to be free from water. Berthollet has shewn, however, that it may retain a considerable quantity of water in combination. He had observed a difference in crystallized barytes, from which the water had been expelled by exposure to the heat of ignition, and barytes prepared by the decomposition of the nitrate by heat, in their power

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* Mémoires de l'Acad. des Sciences, 1783, p. 588.

† Journal de l'Ecole Polytech. Cah. III. p. 300.

‡ Philosophical Magazine, vol. xiv. p. 304.

of neutralizing an acid, the latter combining with a larger quantity of an acid to form a neutral salt than the former. This he found to be owing to the former retaining a portion of water combined with it, and accordingly, in exposing it to heat with iron filings, a large quantity of hydrogen gas was procured. The quantity of water he estimates at 9 *per cent.* In this state, then, it is hydrate of barytes; it appears to be nearly the same with that which is obtained by adding water to the barytes prepared from the decomposition of the nitrate by heat, sufficient to reduce it to a dry powder. When a smaller quantity of water is added, the porous mass from the ignited nitrate absorbs it rapidly, and with much heat, but it rather hardens than falls to powder: this appears to be a hydrate with a smaller proportion of water. And it is not certain even that the barytes procured from the decomposition of the nitrate is the real earth: it too may contain water. On the other hand, the powder formed by the slaking of barytes from exposure to the air appears, from the great increase of weight gained in the process, to contain still more water than the barytes reduced to powder by the immediate affusion of water: and the crystallized barytes contains a still larger quantity. The powerful affinity of barytes to water has an important effect in some of its chemical relations. Thus, some of its compounds with acids, particularly the carbonic, cannot be decomposed by heat unless the due proportion of water be supplied.

Barytes is soluble in water, and since the method of obtaining it in a state of purity has been discovered, its solubility is found to be much greater than had formerly been supposed. This, as well as the crystallization of this earth, were observed by Dr Hope in his researches on strontites. If the hydrate of barytes, or dry powder formed by the slaking of the ignited barytes by sprinkling water on it, be covered with water, it dissolves in it, and forms a congeries of transparent needle-like crystals: cold water dissolves, according to Vauquelin, a twenty-fifth part of its weight: boiling water nearly its own weight: the latter solution deposites, on cooling, prismatic crystals, which efflóresce and fall to powder, when exposed to the air *. These crystals are described by Dr Hope as being, when well formed, flat six-sided prisms acuminated by four planes: they are transparent, but become opaque and white from exposure to the air, losing about 30 *per cent.* of weight. When heated, they undergo the watery fusion, and, as the heat is continued, the water is dissipated, and leaves the barytes in a white powder, with a loss of weight of about one-half. Dr Hope found the crystallized barytes to be soluble in 17.5 of water, at the temperature of 60 †, and in almost any quantity of boiling water.

The solution of barytes has an acrid taste: it changes the vegetable colours to a green. Exposed to the air it absorbs carbonic acid more quickly than lime-water.

According to Vauquelin, barytes is soluble in alkohol, though other chemists have denied to it this property.

Barytes exerts little action on the alkalis, though with the fixed alkalis it may be fused into a species of frit. With borax or phosphate of soda, it forms a transparent glass.

This earth exerts affinities to several of the others. It has the power even of communicating solubility to those that are least soluble. Thus by fusion with silex, a compound is formed soluble in all the acids, even the weakest; and when barytes and alumina, in equal parts, are boiled in water together, both are dissolved. Barytes precipitates silica from its alkaline solution, by uniting with it. It appears to exert no affinities in the humid way to lime, or to magnesia: and even by fusion does not enter into combination with them, or with alumina, at least mixtures of them do not fuse in the most intense heat. Barytes and

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* Nicholson's Journal, 4to, vol. i. p. 557.

† Edinburgh Philosophical Transactions, vol. iv. p. 58.

silica fuse in various proportions, and form a green glass or enamel. Ternary mixtures of these earths are more fusible †. It combines with some of the metallic oxides.

Barytes combines with sulphur by fusion; the sulphuret is of a reddish brown colour, and melts easily; it decomposes water rapidly, producing sulphuretted hydrogen, which combines with the barytes. The hydro-sulphuret of barytes is also formed by transmitting sulphuretted hydrogen gas through water, in which barytes is suspended: it is abundantly soluble. When barytes and sulphur are boiled together in water, the barytes renders soluble about one-fourth of its weight of sulphur, and a liquor is formed of a yellowish red colour, which, when concentrated, deposites crystals of the form of hexaedral prisms. These, according to Berthollet, consist of hydro-sulphuret of barytes. A similar crystallization is obtained when the residuum of the mixture of sulphate of barytes and charcoal powder, which has been exposed in a covered crucible to a red heat, is lixiviated with boiling water, and the liquor is allowed to cool. It might be supposed that in both cases these crystals consist of sulphuretted hydro-sulphuret of barytes: yet they scarcely appear to contain any excess of sulphur, but to consist of sulphuretted hydrogen and barytes alone. The solution remaining after the crystallization contains an excess of sulphur, and seems therefore to be the solution of the sulphuretted hydro-sulphuret. The crystals give out, when acted on by an acid, a large quantity of sulphuretted hydrogen, without any deposition of sulphur. They are white, transparent, and of a silky lustre.

Barytes unites with phosphorus, when the combination is promoted by heat, forming a compound of a dark colour, which decomposes water, producing phosphuretted hydrogen. It acts on none of the metals, but unites with

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† Kirwan's Mineralogy, vol. i. p. 57. &c.

some of the metallic oxides by fusion, and, in the humid way, Vauquelin having remarked, that when barytic water is added to solutions of nitrate of silver or lead, so as to precipitate the oxide, this precipitate is re-dissolved, on adding a new portion of barytic water.

Barytes combines with the acids; the combination appears to be effected with greatest facility when it is in the state of hydrate; hence a peculiarity of its native carbonate, that it does not effervesce from the action of an acid, unless the acid is in a certain degree of dilution, and that the presence of water favours the escape of its carbonic acid by heat. In power of attraction, it has been supposed to be superior to the alkalis, or any of the other earths, as it decomposes their neutral salts. This, however, according to the doctrine of Berthollet, already explained, is owing to the great insolubility of the salts of barytes; and this apparent superior attraction is to be observed only in relation to those acids with which it forms insoluble compounds. With regard to those with which it forms soluble salts, as, for example, muriatic or nitric acid, the experiments of Anfrye and D'Arcet have shewn *, that no such superiority in the force of the affinity exerted by barytes exists; it merely produces partial decompositions of the salts of these acids, and the alkalis precipitate it from these salts, at least if added to their saturated solutions, for otherwise the solubility of the barytes prevents its separation, as it does also if the salt is very soluble; and accordingly, it is not thrown down from a solution of the muriate, by a pure alkali. In the capacity of saturation, or power of neutralizing the acids, it is inferior to the other alkalis and earths.

The barytic salts are in general insoluble, or at least of very sparing solubility. Those of them which are soluble, are chiefly the nitrate, muriate, acetate, tartrate, and super-oxalate. These are easily detected by the a-

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* Annales de Chimie, tom. xlix. p. 85.

bundant precipitate which they afford on the addition of a few drops of sulphuric acid, or of a concentrated solution of any sulphate. They communicate to alkohol the property of burning with a yellow flame. Their taste is acrid and metallic, and they are poisonous.

Carbonate of Barytes exists native, and is prepared artificially, by adding carbonic acid to barytic water, or by decomposing muriate of barytes by an alkaline carbonate. In its native state it occurs massive, of a sparry texture, or crystallized in hexaedral prisms, or in pyramids. It falls down in its artificial production as a white powder, of considerable specific gravity; it is not soluble in water in any appreciable quantity, but is dissolved in small quantity when the water is impregnated with carbonic acid. This compound is differently affected by heat, according as it is in its native state, or has been artificially prepared. From the latter the carbonic acid is easily and completely expelled, while from the former its expulsion is difficult: it was even stated by Withering and Pelletier, that it does not part with its carbonic acid in the most intense heat. Dr Hope shewed that this is an error. It is difficult, indeed, to decompose it by heat in a clay crucible, as the barytes, and the earth of the crucible, act as mutual fluxes, and the crucible is corroded; but in a crucible of black lead, he found the carbonic acid to be expelled on applying a very high and continued heat by a smith's forge; and this even from the carbonate in a considerable mass, so that the carbonaceous matter of the crucible could have little effect in favouring the operation by any decomposition of the acid. Klaproth, however, could expel it only partially in a platina crucible. The difference in the facility of decomposition between the native and artificial carbonate, is evidently owing to the influence of water; the former appears to be free from water, while the latter retains a portion of it, which favours the expulsion of the carbonic acid gas. Accordingly, if watery vapour be transmitted over the native carbonate when it is exposed to heat, the carbonic acid is more easily expelled from it. This influence of water is even to be observed in the action of an acid upon it: if the native carbonate be put into strong muriatic acid, it does not suffer any change; the artificial carbonate effervesces strongly; and if the muriatic acid, in which the native carbonate is immersed, be diluted with two or three parts of water, an effervescence also commences from the disengagement of carbonic acid gas. These facts were formerly explained on the supposition, that a portion of water is essential to the constitution of carbonic acid gas. But this gas contains no combined water; and the effect is probably to be ascribed to the relation of water to barytes. Its affinity counteracts the affinity of the carbonic acid, and therefore favours its expulsion by heat; or according to a different view, the hydrate of barytes combines more readily than the pure earth with acids. The native carbonate, according to Withering, is composed of barytes 78.6, carbonic acid 20.8; according to Klaproth, of barytes 78, and carbonic acid 22. Berard assigns also these last proportions from experiment; Bucholz makes them 79 and 21; and Berzelius 78.4, and 21.6. The artificial carbonate dried at nearly a red heat, consists, according to Aikin, of barytes 78.33, carbonic acid 21.67; and according to Mr J. Thomson, of barytes 78.25, carbonic acid 21.75. According to Berthollet, the artificial compound obtained by the usual method is a sub-carbonate, in which 100 of barytes are combined with 27.07 of carbonic acid, a proportion nearly the same as those above; and to form the neutral carbonate, double this quantity of acid would be required *.

Nitrate of Barytes is obtained by dissolving either pure barytes or the native carbonate in nitric acid: if the acid is strong, a congeries of crystals is formed; if dilute,

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* Mémoires d'Arcueil, tom. ii. p. 478.

the solution, by evaporation, affords crystals in octaedrons, or in small brilliant plates: its taste is styptic and pungent: it is not much altered by exposure to the air: its crystals are soluble in 10 or 12 parts of water at 60°, and in 3 or 4 parts of boiling water; the latter solution crystallizing on cooling. It is decomposed by heat; from the strength of attraction of the base to the acid, little of the latter is expelled in an undecomposed state, but it is converted into oxygen and nitrogen gases. It detonates feebly with inflammable bodies. According to Kirwan, it consists of barytes 57, acid 32, and water 11; according to Vauquelin, of barytes 50, nitric acid 38, and water 12 *. In the real salt, according to Berzelius, 100 of acid are combined with 140 of base.

Sulphate of Barytes. This compound is formed when barytes is presented to sulphuric acid, in whatever state of combination either the earth or the acid may previously have been. Though it exists in nature crystallized, it can be obtained artificially only in the state of powder. Its native crystals are bevelled tables, or flat prisms of six sides. Its specific gravity in this state is 4.4. It is insoluble in water, or at least cannot be dissolved in any appreciable quantity. It is perfectly tasteless. It is fused by a strong heat: a small fragment of it is melted by the blowpipe into an opaque globule. When heated with carbonaceous matter, its acid is decomposed, and sulphuret of barytes is formed. It is partially decomposed when heated with several neutral salts, as with carbonate of potash or soda; more sparingly, with muriate of soda, and almost completely with muriate of lime when the two salts are mixed in equal proportions. The determination of its composition is of much importance, as it often forms the basis of the estimation of the quantities of sulphuric acid in compounds. The statements from different authorities

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* Journal de l'Ecole Polytech. Cah. III. p. 581.

have been very various, the proportion of barytes having been stated at 66 or 67, and so high also as 76 or 78, discordances arising chiefly from the presence of water in ignited barytes, in proportions variable, according to the mode of preparation, introducing in the synthetic experiment inaccurate estimates of the quantity of real barytes. The experiments of Black, Withering, Klaproth, Richter, Rose, Bucholz, Aikin, J. Thomson, and Berthier, correspond, with the variation of a few decimal parts, in fixing the proportions at 66 of barytes and 34 of acid [*], and these are the precise proportions by Berzelius, and adopted in Dr Wollaston's scale.

Barytes can be combined with an excess of sulphuric acid, by boiling sulphuric acid on sulphate of barytes in powder; a transparent solution is formed, which displays a congeries of prisms; it is decomposed, and the neutral sulphate precipitated, on the affusion of water.

Sulphite of Barytes is formed by transmitting sulphurous acid over carbonate of barytes, or decomposing any of the sulphites by the addition of a solution of a barytic salt. It is in the form of a powder, or of very small tetraedral crystals; has a taste slightly sulphureous; is scarcely altered by exposure to the air, if it is in a dry state; and is as insoluble as the sulphate: it is decomposed by heat, sulphur being sublimed from it.

Phosphate of Barytes is formed, by decomposing muriate or nitrate of barytes, by neutral phosphate of soda or ammonia. It is an insipid white powder, of considerable specific gravity: is insoluble in water; but becomes soluble from an excess of acid; is fusible at a high temperature, and is not decomposed by exposure to heat mixed with carbonaceous matter. According to Berzelius [†], it

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[*] Nicholson's Journal, vol. xxii. p. 304. vol. xxiii. p. 174, 270. Mémoires d'Arcueil, tom. ii. p. 44.

[†] Annals of Philosophy, vol. ix. p. 44.

consists of 68.2 of barytes, and 31.8 of phosphoric acid. The same chemist found, that when this phosphate is digested in liquid phosphoric acid, until as much of it as possible is dissolved, the solution afforded, by slow evaporation, crystals of a salt similar in appearance to the muriate, of a taste slightly acid, and which reddens litmus. It swells when exposed to heat. Water removes the excess of acid. It contains exactly twice the quantity of acid that is contained in the neutral phosphate; and is therefore BI-PHOSPHATE OF BARYTES. In its crystallized state, it consists of barytes 46.46, phosphoric acid 42.54, water 11. When this salt in solution is poured into alkohol, a bulky precipitate falls down, which when washed with alkohol, and dried, forms a light white powder. Berzelius found it to consist of 60.87 of base, and 39.13 of acid. It contains, therefore, 1½ as much acid as the neutral compound, or is SESQUI-PHOSPHATE OF BARYTES.

PHOSPHITE OF BARYTES may be formed, by adding phosphorous acid, or an alkaline phosphite, to a solution of barytes, or of the muriate or nitrate of this earth. It is a white powder, insipid, and very sparingly soluble in water: it melts before the blow-pipe into an opaque globule, and is luminous during its fusion. According to Berzelius, when formed by dropping muriate of barytes into a solution of phosphite of ammonia, it adheres in minute crystals, after 24 hours, to the sides of the vessel. Vauquelin stated its composition at 51.3 of barytes, 41.7 of acid, and 7 of water. Berzelius finds it to consist of 67.24 of base, 24.31 of acid, and 8.45 of water.

HYPO-PHOSPHITE OF BARYTES is formed, according to Dulong, when phosphuret of barytes is dropt into water. It remains in solution, while phosphate of barytes is precipitated, and is so soluble, that it can scarcely be crystallized.

BORATE OF BARYTES is formed by adding boracic acid to barytic water, or by adding a solution of a neutral borate to one of muriate of barytes. A white powder is precipitated, which has been said to be insoluble, but which, according to L. Gmelin, has nearly the same solubility as sulphate of lime. It is more soluble in hot than in cold water. It intumesces on exposure to a red heat, and is converted into a greenish vesicular mass. It consists of barytes 54.7, boracic acid 45.3 [*].

Muriate of Barytes. When dry and pure barytes is heated in muriatic acid gas, the gas is condensed, a portion of water is liberated, and the saline product constituting the muriate is formed. The mutual action is farther attended with a striking phenomenon, observed by Chevreul [†], the evolution of light producing a fine red glow, and the production of much heat, so that the muriate is fused. When oxymuriatic gas is transmitted over the dry earth heated, oxygen gas is liberated, and the same saline product is obtained. According to the old doctrine, the oxygen is derived from the acid, the muriatic acid combining with the earth; according to the other, it is disengaged from the barytes, the chlorine combining with the barium. The salt is usually formed by dissolving the native carbonate in diluted muriatic acid; or by adding muriatic acid to the liquor formed by the lixiviation of the product of the decomposition of sulphate of barytes by ignited charcoal, taking care to produce neutralization. The solution in either case is evaporated, to afford crystals: the crystals are quadrangular tables, bevelled on the edges: they are soluble in 5 parts of cold water; and are more soluble in hot water, though not much so; and the solution therefore does not crystallize on cooling. A singular result takes place, in consequence of the greater solubility of this salt than of the nitrate. If concentrated nitric acid be dropt into a saturated solution of it, a precipitate is formed, which is nitrate of barytes. The same result had

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[*] Annals of Philosophy, vol. ix. p. 48.

[†] Annales de Chimie, tom. lxxxiv. p. 285.

been remarked by Dr Hope to occur with regard to strontites. Muriate of barytes is soluble in alkohol, and gives to the flame of the alkohol in burning a yellow tinge. From exposure to the air, it suffers no alteration. When heated, it decrepitates, and loses its water of crystallization, but is not decomposed. The determination of its decomposition is of importance, as it is often employed as a re-agent in analysis. According to Kirwan, it consists, when crystallized, of barytes 64, acid 20, water 16; according to Vauquelin, of barytes 60, acid 24, water 16. Mr Aikin found the crystallized salt to contain 62.47 of barytes, 22.93 of acid, and 14.6 of water; and the ignited muriate to consist of 73.14 of barytes, and 26.86 of acid. Berthier states the composition of the former at 64 of barytes, 21 of acid, and 15 of water; and of the latter at 75.3 of barytes, and 24.7 of acid. These last proportions nearly, are assigned by Rose. Berzelius states them at 23.35 of acid, 61.85 of base, and 14.8 water; and in the real salt at 74.25, and 25.75, the mean nearly of those that may be regarded as most accurate. According to the doctrine which considers this salt as a chloride, it consists of 66.04 of barium, and 33.96 of chlorine.

Hyper-oxymuriate, or Chlorate of Barytes, is obtained by passing oxymuriatic gas through water in which barytes is diffused; hyper-oxymuriate and muriate of barytes are formed: and as these two salts have nearly the same degree of solubility, they are not easily separated: according to a method, however, proposed by Chenevix, the latter is abstracted by boiling the solution with phosphate of silver, dissolved in distilled vinegar: this decomposes it, forming phosphate of barytes and muriate of silver, which are both precipitated, while the hyper-oxymuriate of barytes remains dissolved. Chenevix merely remarks of it, that it has the general properties of the hyper-oxymuriates, and that it consists of 42.2 of base, 47 of acid, and 10.8 of water. Vauquelin, in the account he has given of the Chlorates *, states, that it crystallizes in four-sided prisms; its taste is harsh and styptic; it is soluble in about four parts of water at 50; and is insoluble in alkohol; it yields no precipitate from the addition of nitrate of silver. It is decomposed by heat, and affords oxygen, amounting to 39 from 100 of weight; the residue is alkaline.

FLUATE OF BARYTES. Pure fluoric acid causes a flocculent precipitate when added to a solution of barytes, which is the fluate; and the same compound is formed on adding the nitrate or muriate of barytes to fluate of potash. An excess of fluoric acid renders it soluble, and nitric and muriatic acids dissolve it with equal facility †.

SILICEO-FLUATE OF BARYTES. On adding nitrate or muriate of barytes to a solution of siliceo-fluoric acid, the liquor remains at first clear, but after a few minutes it becomes turbid, and deposites a number of small crystals, very hard, insoluble in water, and in nitric and muriatic acids, and which, when calcined with lamp-black, suffer no change. These crystals, Gay Lussac observes, are no doubt the triple compound of fluoric acid, barytes, and siliceous earth ‡.

HYDRIODATE OF BARYTES crystallizes in slender prisms, similar to the crystals of muriate of strontites. Though very soluble in water, they are but feebly deliquescent. When heated in a close vessel even to redness, this salt does not melt, nor is its state of neutralization altered; but if heated under exposure to the air, or to oxygen gas, it is decomposed, vapours of iodine arise, and it remains alkaline. Even from exposure to the air without heat, it gradually suffers change from the decomposition of the hydriodic acid by the oxygen of the atmosphere, and the consequent evolution of iodine. It consists, accord-

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* Annales de Chimie, tom. xcv.

† Gay Lussac, Recherches Physico-Chimiques, tom. ii. p. 24.

‡ Recherches Physico-Chimiques, tom. ii. p. 25.

ing to Gay Lussac, of 100 of hydriodic acid, with 60.622 of barytes *.

Oxiodate of Barytes. This salt is obtained by adding iodine to barytic water, or by decomposing muriate or nitrate of barytes by an alkaline oxiodate. It falls down in powder; in drying it becomes farinaceous. Though heated to 212°, it does not part with the whole of its water, a portion being expelled at a higher temperature. 100 parts of water at 212 dissolve 0.16 of it, and at 60 only 0.03 parts; it is not fusible, and does not deflagrate, like some of the other salts of the same genus, on burning charcoal. It is decomposed by a heat sufficiently elevated, the products being barytes, oxygen, and iodine. It is composed, according to Gay Lussac, of 100 of oxiodic acid, and 46.340 of barytes †.

The salts which barytes forms with the vegetable acids, fall to be considered under their history. Those with oxalic and citric acid are of very sparing solubility, so as to be precipitated at their formation; but they are rendered soluble by an excess of acid. With tartaric acid it forms a soluble salt; with gallic acid one so little soluble, that it falls down in flocculi. Prussic acid has been supposed to precipitate it, at least when added in the state of an alkaline prussiate, such as that of potash, to solutions of its salts; and this was regarded as in some measure assimilating it with the metals, the solutions of which are generally precipitated by this test. Meyer and Klaproth observed, however, that no precipitation from the solutions of barytes takes place, unless when the prussiate employed is contaminated with a sulphate ‡. Dr Henry shewed, that although no immediate precipitate is formed,

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* Annales de Chimie, tom. xci. p. 57.

† Ibid. tom. xci. p. 81.

‡ Analytical Essays, vol. i. p. 593.

on the addition of prussiate of potash to a barytic salt, when the prussiate is pure, yet in a few hours crystals are deposited from the liquor, consisting of prussiate of barytes; which proves, that the salts have, in part at least, exchanged their principles*: but this, as Guyton has remarked, is not peculiar to this earth; a similar exchange happening with the salts of other earths and alkalis †. Dr Henry observes, that the same crystals are formed from barytic water added to the prussiate.

CHAP. II.

OF STRONTITES AND ITS BASE.

The native carbonate of this earth, a mineral found at Strontian in Argyleshire, had been known to mineralogists, but had been considered as a variety of carbonate of barytes, and this even by Pelletier, by whom it had been submitted to chemical analysis ‡. Dr Crawford, or rather his assistant Mr Cruickshank, had observed the difference in the solubility of its muriate from that of barytes ||. Dr Hope had observed differences between the two minerals, which led him to conclude, that the Strontian mineral did not belong to the barytic genus: and in 1792 he executed a series of experiments, afterwards published, from which he inferred, that it contains an earth before unknown, to

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* Nicholson's Journal, 4to, vol. iv. p. 50.

† Ibid. 8vo, vol. iii. p. 196.

‡ Mémoires de Chimie, tom. i. p. 586.

|| London Medical Communications, vol. ii.

which, from the name of the place where it had been found, he gave the denomination of Strontites *. Klaproth, unacquainted with Dr Hope's experiments, had examined the native carbonate: Pelletier, too, resumed his investigation of it; and, by both these chemists, its existence as a peculiar earth was established †. It has been since found native, combined with sulphuric acid.

Strontites may be obtained by processes similar to those by which barytes is procured, either from the native sulphate or carbonate. Dr Hope found, that the native carbonate is decomposed by an intense heat, and thus obtained strontites, separating it from any insoluble matter by the action of water. The decomposition may be aided by exposing the carbonate to heat in mixture with charcoal powder. The nitrate exposed to heat in a platina crucible, is decomposed so as to afford its base, with still more facility than the nitrate of barytes. From the native sulphate, the strontites may be procured by the same process as that by which barytes is obtained from its sulphate.

The decomposition of this earth is attained by the same modes of galvanic analysis as those applied to the other earths. By negatively electrifying it in contact with mercury, Davy found the phenomena, denoting the decomposition of the earth and the addition of metallic matter to the mercury, to take place. And by distilling the quicksilver from it, he obtained the metallic base, though in an imperfect manner; hence its properties have been scarcely examined. It had the general appearance of the base obtained from barytes, and by exposure to the air was converted into strontites, absorbing oxygen, and gaining weight in the process. Like barium, it sinks in sulphuric acid, and is therefore of considerable specific gravity. He

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* Edinburgh Philosophical Transactions, vol. iv.

† Klaproth's Analytical Essays—Mémoires de l'Inst. National, tom. i. p. 88.; or Nicholson's Journal, 4to, vol. i. p. 518.

named it Strontium. The proportion in which it combines with oxygen, so as to form the earth, could not be directly determined. But it may be indirectly inferred, from the principle already explained with regard to barytes, (page 14.). From the analysis of muriate of strontites, by Davy, the proportion of oxygen in the earth was inferred by Berzelius to amount to 14.09 in 100 parts. Stroymeyer has lately analysed the carbonate with great care; it is composed of 70.313 of base, and 29.687 of acid. From this it follows, that the earth contains 15.331 *per cent.* of oxygen, and of course consists of this quantity of oxygen with 84.669 of strontium. In conformity to this, the equivalent weight of strontites on the scale of Wollaston is 65.228, and of strontium 55.228 *. Dr Wollaston had stated that of strontites at 69.

STRONTITES, or STRONTIA, as some name it, obtained by the usual processes, is in masses of a greenish-grey colour, and porous texture; its specific gravity is 1.6; it has a pungent acrid taste, rather less harsh than barytes; the powder, however, raised in its pulverization, is very irritating. It is not poisonous like that earth. It can be obtained in crystals. Dr Hope formed them by throwing into boiling water the recently calcined carbonate: on allowing the solution to cool, crystals were deposited; their form being a thin quadrangular table, sometimes bevelled at the extremities: they are transparent, but become very quickly white and efflorescent, on exposure to the air, from the loss of part of their water of crystallization. They undergo the watery fusion at a dull red heat, and at length remain in the state of a white powder; 100 parts losing by the expulsion of water 68 of weight. This powder is probably a hydrate: a similar powder is obtained by the affusion of a small quantity of water on the ignited strontites. It is not

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* Annales de Chimie et Physique, tom. iii. p. 397.

fused by a very strong heat: the flame of the blowpipe does not affect it, further than rendering it phosphorescent.

Strontites is soluble in water, but much less so than barytes. The crystals require 50 parts of water at 60° for solution; boiling water dissolves nearly half its weight. The strontites not in a crystallized state, is, of course, more sparingly soluble; it requires nearly 200 parts of water at 60°. Its solution changes the vegetable colours to a green. Strontites in crystals is also soluble in alkohol, though sparingly.

Strontites exerts no marked action on the alkalis, nor on barytes or lime. With some of the other earths, particularly with silica and alumina, it combines.

It combines with sulphur, by exposing a mixture of equal parts of them to heat in a covered crucible, or by decomposing sulphate of strontites by charcoal at a red heat. From the observations of Berthollet it appears, that by raising the heat, and continuing its application, the greater part of the sulphur may be expelled. The sulphuret is dissolved by water; the solution acquiring a yellow colour, and being a sulphuretted hydro-sulphuret: crystals are at the same time formed in it, which are colourless, and which, like the analogous combinations with barytes, appear to be the hydro-sulphuret, as, when decomposed by an acid, sulphuretted hydrogen is disengaged without any deposition of sulphur. Their properties are similar to those of hydro-sulphuret of barytes. Strontites also combines with phosphorus by the usual process, and forms a compound which decomposes water.

This earth combines with all the acids. Its salts have a similar relation to solubility with the barytic salts,—the muriate, nitrate, and acetate, being abundantly soluble; the others, and more particularly the carbonate, sulphate, phosphate, and oxalate, being insoluble, or of sparing solubility. The strontitic salts, however, have in general more solubility than the barytic salts: hence sulphuric acid, which is so delicate a test of barytes, is one much less so of strontites, as its salts are not precipitated by it, if they are in dilute solutions; and it affords, on the other hand, a much less delicate test of this acid. Two tests more particularly distinguish the two earths in their saline combinations. 1*st*, When the salts of strontites are precipitated by oxalic acid, the precipitate is not re-dissolved by an excess of acid, as that from the barytic salts is; and if dilute solutions of these salts are submitted to the action of this test, those of strontites give a precipitate, while those of barytes afford none: 2*dly*, The watery solution of strontites is not, like that of barytes, precipitated by malic or by gallic acid. It is stated also, that succinic acid and arsenious acid precipitate barytes, but not strontites, as they form with the latter soluble salts. Arsénic acid combined with strontites to neutralization, forms a compound of sparing solubility, which with an excess of acid is rendered soluble. Those of the strontitic salts which are soluble in alkohol, give it the property of burning with a purple coloured flame; and paper dipt in their watery solution and dried, or the wick of a candle on which a little of the salt is put, burns with the same flame. The earth itself has this property, but in all these cases the presence of a little humidity is necessary, as Dr Hope remarked, to the production of the colour. The strontitic salts are in general decomposed by barytes; barytic water, for example, added to a strong solution of the muriate, causes an immediate precipitation of strontites; and the decomposition, according to Fourcroy and Vauquelin, is complete. The muriate and nitrate are even decomposed by the fixed alkalis, strontites in minute crystals being precipitated when potash or soda is added to their solutions; but the decomposition, as Dr Hope shewed, is only partial. In this respect strontites differs from barytes, and the effect evidently arises from the sparing solubility of the former. It attracts from the alkalis those acids with which it forms insoluble compounds. The properties of the individual strontitic salts have been investigated principally by Dr Hope *, and by Vauquelin †, and lately their analysis has been executed by Stromeyer ‡.

Carbonate of Strontites exists native, and is formed on adding carbonic acid, or a solution of an alkaline carbonate, to a solution of strontites, or of a strontitic salt. Being insoluble it is precipitated. With an excess of acid it becomes soluble. The native carbonate occurs massive, of a radiated texture, or crystallized in prisms. The artificial carbonate, like that of barytes, is more easily decomposed than the native carbonate. The latter is decomposed with effervescence by acids, without requiring so much dilution with water as is necessary to the decomposition of carbonate of barytes, but still dilution to a certain extent favours the effects. The composition has been variously estimated. The strontian spar Dr Hope found to lose more weight from exposure to heat, than by solution in acids, the loss in the former being 38.79 *per cent.*, and in the latter 30.20: the difference might be inferred to arise from the expulsion of water, and from this he stated the proportions at 61.21 of earth, 30.20 of acid, and 8.59 of water. Pelletier assigned proportions almost precisely the same. Klaproth found, however, scarcely any water: he stated them at 69.5 of strontites, 30 of acid, and 0.5 of water. Berard fixed them at 73.6, and 26.4. Stromeyer lately executed the analysis with much care. He found that the quantity of carbonic acid could not be found with accuracy from the loss of weight by its solution in acids, but only by collecting it; and as the result of this mode, he determined the composition of the pure dry carbonate to be strontites 70.313, carbonic acid 29.687,—a proportion of

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* Edinburgh Philosophical Transactions, vol. iv.

† Journal des Mines, No. xxxvii.

‡ Annales de Chimie et Physique, tom. iii. p. 395.

carbonic acid almost the same as that found by Dr Hope and by Klaproth, from solution in acids. Stromeyer found the native carbonate to be of the same composition, containing only usually a small quantity (about 2 *per cent.)* of carbonate of lime. It appears therefore to contain no water.

Nitrate of Strontites. If concentrated nitrous acid be poured on native carbonate of strontites, no action ensues in the cold; but if heat be applied, or water be added, solution with effervescence takes place: about an equal weight of water, it was remarked by Dr Hope, is necessary; and if less be used, though the solution and effervescence commence, they soon cease. With rather an under proportion of water, part of the salt crystallizes as it forms. It may also be obtained by adding nitric acid to the liquor prepared from the decomposition of the native sulphate by ignited charcoal, evaporating to dryness to expel any excess of acid, re-dissolving, and crystallizing. The crystals of this salt are either hexaedral pyramids, or octaedrons, with the apex of the pyramid, or the angles truncated. Its taste is pungent; it does not require more than an equal weight of water at 60° for its solution; and at 212° it dissolves in little more than half its weight; the latter solution depositing a confused mass of crystals on cooling. It is deliquescent in a humid atmosphere; in a dry atmosphere it effloresces. It decrepitates, then melts, and lastly is decomposed by heat, and gives more nitrous acid vapour than nitrate of barytes decomposed in the same way, owing to its acid being retained by a weaker force. It deflagrates feebly, when laid on burning fuel. According to Kirwan, it is composed of 36.21 of base, 31.07 of acid, 32.72 of water: according to Vauquelin, it is composed of 47.6 of base, 48.4 of acid, and 4 of water. Stromeyer states as its composition, strontites 49.38, nitric acid 50.62. It contains, he adds, no water of crystallization, and the small quantity found by Vauquelin is merely mechanically lodged in the crystals. There is reason to believe, however, that a nitrate exists containing combined water, which has the property of efflorescing on exposure to the air; and it must be to this nitrate that the analysis of Kirwan applies.

Sulphate of Strontites is in the form of a white powder, insipid, and nearly insoluble in water; requiring at least, according to Dr Hope, 4000 parts for its solution. It combines with an excess of acid, and forms a transparent solution, which does not crystallize so readily as the super-sulphate of barytes; but like that salt is decomposed by water. The native sulphate occurs massive, and crystallized in tables. It consists, according to Clayfield, Klaproth, and Kirwan, of 58 of earth, and 42 of acid; according to Vauquelin, 54 of earth, and 46 of acid: Stromeyer gives as the proportions, 57 of base, and 43 of acid.

Phosphate of Strontites. Phosphoric acid acts weakly on the native carbonate of this earth: the phosphate remains dissolved, while there is an excess of acid; but as this is neutralized, it is deposited in a white powder; it may also be formed by adding a phosphate to muriate of strontites; when perfectly neutral, it is very sparingly soluble in water, requiring about 2000 parts for its solution. It melts into an enamel by the flame of the blow-pipe; giving also a phosphorescent light. According to Vauquelin, it consists of 58.76 of strontites, 41.24 of phosphoric acid. Stromeyer gives as the proportions 63.435 of strontites, and 36.565 of phosphoric acid; and he remarks, that the proportions assigned by Vauquelin do not accord with the capacity of saturation of the acid.

Borate of Strontites. Carbonate of strontites thrown into a hot solution of boracic acid suffers decomposition, a slight effervescence and solution taking place; and as there is an approach to neutralization, a powder is precipitated. A precipitate is also formed on neutralizing the acid by strontitic water. It is scarcely acted on by cold water; boiling water, Dr Hope found, dissolved about a hundred and thirtieth of its weight, and the salt dissolved seemed to be a sub-borate, as the solution changed the colour of violet to a green.

Muriate of Strontites. When strontites is heated in muriatic acid gas, the gas is absorbed, and a portion of water appears; and the same striking phenomenon of the evolution of heat and light, similar to combustion, attends the mutual action, as takes place in the corresponding experiment with barytes *. When heated in oxymuriatic acid gas, oxygen gas is liberated either from the acid, according to the one doctrine, or from the earth according to the other, and muriate of strontites, or chloride of strontium, is formed. The salt is usually obtained from the action of diluted muriatic acid on the native carbonate, or from the addition of the acid to the solution of the hydrosulphuret formed from the decomposition of the native sulphate by charcoal at an elevated temperature. The solution in either mode, by evaporation, affords crystals, which are slender hexaedral prisms. These are deliquescent in a humid atmosphere: they are very soluble in water; one part of water, at 60°, dissolving one and a half, and, in boiling water, they dissolve in any quantity, the water of crystallization itself being sufficient to keep the salt in solution. A singular result happens, on adding to the saturated solution strong muriatic acid; the salt is precipitated in minute crystals, from the acid attracting the water, and thus abstracting its effect as a solvent: nitric acid added to the saturated solution of the muriate, causes an immediate precipitation of minute crystals of nitrate, the inferior solubility of this salt causing its formation, by the influence of the force of cohesion. The muriate is soluble in alkohol. Its crystals exposed to heat lose 42 *per cent.* from the escape of the water: by a red heat, the

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* Chevreul, Annales de Chimie, tom. lxxxiv. p. 286.

salt is fused; but its acid is not expelled. It consists, according to Vauquelin, of strontites 36.4, acid 23.6, water 40. The fused muriate, according to Stromeyer, is composed of strontites 65.585, muriatic acid 34.415. If it be considered as a chloride, it will, according to this estimate, consist of 55.5 of strontium, 44.5 of chlorine.

HYPER-OXYMURIATE OF STRONTITES is prepared by the process similar to that by which hyper-oxymuriate of barytes is formed. Chenevix remarked, that it crystallizes in needles, is deliquescent, and soluble in alkohol; and consists of 26 of base, 46 of acid, and 28 of water. Vauquelin obtained it from the action of chloric acid on carbonate of strontites; from its great solubility, he found it difficult to procure it in crystals. It fuses on red hot charcoal, and gives a fine purple flame.

FLUATE OF STRONTITES is formed in the same way as fluate of barytes, and like that salt is precipitated in flocculi insoluble in water, but rendered soluble by an excess of fluoric acid, and dissolved by nitric and muriatic acids. It is uncertain if the Siliceo-fluate of strontites can be formed *. The liquid siliceo-fluoric acid has been said scarcely to act on the native carbonate: added to a solution of the earth in water, it occasions a milkiness from the production of a compound of sparing solubility.

HYDRIODATE OF STRONTITES is a very soluble salt; it melts below a red heat; if heated in close vessels, it becomes only slightly alkaline; but if atmospheric air or oxygen be admitted, dense vapours of iodine immediately arise, from the action of the oxygen on the hydriodic acid †.

OXIODATE OF STRONTITES may be formed in the same way as oxiodate of barytes. It is in small crystals, which viewed through a glass appear to be octohedrons; 100 parts of water dissolve 0.73 of it at 212°, and 0.24 at 60°;

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* Gay Lussac, Recherches Physico-Chimiques, tom. ii. p. 25.

† Gay Lussac, Annales de Chimie, tom. xci.

it gives out water when heated previous to decomposition, and when decomposed yields strontites, oxygen, and iodine *.

With the vegetable acids, strontites forms salts, in a general point of view, analogous to those which barytes forms: those with malic and gallic acid are more soluble.

Though strontites has, in a number of its properties, a considerable resemblance to barytes, yet in others it is so different, as to prove it to be a substance altogether distinct. It is distinguished by its less solubility in water; by the different form of its crystals; by the greater solubility of a number of its salts, particularly of the nitrate and muriate; as well as by the difference in their crystalline forms, and in other properties; by its salts being decomposed by barytes; and by the blood-red colour which they give to the flame of combustible bodies. The tests by which they are most easily determined in their saline combinations, have been stated above.

CHAP. III.

OF LIME AND ITS BASE.

This earth is found in great abundance in nature: it is the principal constituent part of marble, lime-stone, plaster-stone, marl, and many other fossils. It is contained in all spring and river water: it exists in the water of the ocean; is found in vegetables; and is the basis of the shells, bones, and other hard parts of animals.

To obtain it uncombined, white marble, or the shells of

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* Gay Lussac, Annales de Chimie, tom. xci.

marine animals, are exposed to a strong heat, sufficient to expel the carbonic acid with which the lime is combined. As thus obtained, however, it may not be perfectly pure; that from marine shells may have an intermixture of phosphate of lime; and even those marbles which appear most pure often contain other earths, with which the lime will be mixed. It should therefore be purified by solution in an acid. The process given by Chenevix, is to dissolve white marble in dilute muriatic acid, leaving an excess of lime undissolved: the solution should afford no precipitate with ammonia,—as a proof that neither alumina nor magnesia is present: it is then to be decomposed by a solution of pure carbonate of potash; and the carbonate of lime, which is thrown down, having been well washed with water, is to be exposed to a violent heat in a platina crucible, until it cease to lose weight *. Calcareous Spar, when colourless and transparent, will probably afford, by the expulsion of its carbonic acid by heat, lime perfectly pure.

Lime subjected to the action of galvanism in high intensity, Davy found gave appearances of decomposition; when mercury was submitted along with it to this action, an amalgam was formed; and when the general process, already described as applied to the earths, was applied to lime, this amalgam was readily produced. Exposed to the air, lime was regenerated; and the same effect was immediately obtained by the action of water, hydrogen being evolved, and quicksilver produced. He did not succeed, however, in procuring the metallic base of lime in its insulated state. In the experiment in which the quicksilver had been distilled from it to the greatest extent, the tube broke while warm; "and at the moment that the air entered, the metal, which had the colour and lustre of silver, instantly took fire, and burnt with an intense white light into quicklime." To this base he gave the name of Cal-

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* Memoirs of the Irish Academy, 1802.

cium. The proportion of oxygen with which it combines to form lime, it is obvious from the above statement, could not be directly determined. Berzelius, from the results of the action of water on the amalgam of calcium, inferred, that 100 of the metallic base of lime combine with 38.5 of oxygen; and this corresponds with the determination drawn from the composition of the salts of lime on the principle already illustrated, (page 14.). From the analyses of the sulphate, muriate, and carbonate, it follows as a mean result, that 100 of calcium combine with 39.2 of oxygen; and conformable to this, that 100 of lime are composed of 71.8 of calcium, and 28.2 of oxygen.

Lime when pure is perfectly white: if in a coherent mass, it is moderately hard, brittle, and has a specific gravity of 2.3: it has a pungent bitter taste, and acts powerfully in destroying the cohesion of animal and many vegetable substances: hence the epithet of caustic given to it in this state, as distinguished from the state in which it exists combined with carbonic acid. It changes the vegetable colours to a green. Trommsdorff obtained crystals by boiling four parts of a solution of muriate of lime with one part of lime, which he supposed to be lime; but which are sub-muriate of lime. Gay Lussac has effected the crystallization by exposing lime-water in the exhausted receiver of an air-pump, along with sulphuric acid. The evaporation of the water is thus effected very slowly, and without agitation, and the lime is obtained in the form of six-sided prisms *.

Lime is nearly infusible: if not perfectly free from other earths, it vitrifies by a very strong heat, but, if pure, it undergoes no agglutination in the focus of the most powerful burning mirror. Lavoisier could not melt it by the heat of burning charcoal excited by oxygen: both in his and Guyton's trials, it only formed a kind of enamel on

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* Annales de Chimie et Physique, tom. i. p. 334.

the edges when exposed in small fragments to the flame. Even in the stronger heat excited by oxygen and hydrogen gases kindled, its fusion is effected with difficulty: black vitreous globules were obtained from exposing it to the flame on charcoal, in Mr Hare's experiments; in Dr Clarke's late experiments, the fusion was more complete, a perfect glass being obtained.

When water is poured on quicklime, it is absorbed with a hissing noise, the lime splits, and falls into a fine powder, which is perfectly dry: and so much caloric is evolved, as to convert a portion of the water into vapour. This process is the slaking of lime: the phenomena accompanying it are owing to the strong attraction of lime for water: and as in this combination the water passes to the solid state, a large quantity of caloric is evolved. Pelletier observed, that in this operation the lime is often phosphorescent, or light is disengaged. The dry powder is a hydrate containing nearly one-fourth of its weight of water: slaked lime freed from extraneous moisture by exposure to a moderate heat, being found by Mr Dalton to be composed of 100 of lime with 33.3 of water *.

Lime is slaked by exposure to the air, by gradually attracting moisture. It gains in weight 33 *per cent.*

At the temperature of 60, water dissolves about $\frac{1}{750}$th of its weight of lime. Mr Dalton states the fact, that more is dissolved by cold than warm water: 100 parts of water at 60° dissolving $\frac{1}{778}$ of lime, or $\frac{1}{584}$ of hydrate of lime, while at 212° it dissolves only $\frac{1}{1270}$ of the former, or $\frac{1}{952}$ of the latter †. This circumstance is extremely singular; augmented solubility from cold is contrary to all analogy, as well as to the principle on which the relation of temperature to solution depends.' It appears, too, that lime exists in its caustic state in solution in some mineral springs,

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* Chemical Philosophy, vol. i.

† Ibid. p. 509.

in which it appears to be dissolved in large quantity by the aid of heat, so that it is deposited as the temperature falls. A striking example of this occurs in the water of a hot-bath near Pisa,—the temperature is 110; " the water is so saturated with lime, that on cooling, it deposites a considerable quantity *."

Lime Water, as the aqueous solution is named, is colourless and transparent; has a styptic taste; and changes several vegetable colours to green. On exposure to the air, its surface is soon covered with a pellicle, which thickens till it breaks and falls down; another is formed, and this goes on till the water become nearly tasteless. This change is owing to the lime attracting carbonic acid, and being converted into the carbonate, which is insoluble. A similar absorption of carbonic acid takes place, when lime in powder is exposed to the atmosphere, but much more slowly; and it appears, that in a perfectly dry atmosphere there is scarcely any absorption.

Lime does not appear to exert any affinity to the alkalis in the humid state; nor does it even combine with them by fusion; a mixture of lime with soda remaining without aggregation, in the heat excited in burning charcoal by a stream of oxygen gas †.

It exerts affinities to several of the other earths. With barytes or strontites it does not combine, but it unites either in the humid way, or by the aid of heat, with magnesia, alumina, and silica; to these combinations is probably in part owing the induration of mortar. Mortar, in particular, which becomes hard under water, owes this quality, according to Descostils, to the presence of silica in the limestone from which it is prepared; and in proof of this, he adds the fact, that in limestones of this kind, the siliceous earth does not dissolve in acids before calcination, while

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* Journals of the Royal Institution, vol. i. p. 260.

† Journal de l'Ecole Polytech. Cah. III. p. 302.

after calcination it dissolves almost entirely, being rendered soluble by combination with the lime *.

Lime is capable of combining with the simple inflammables. Its combination with carbon is indeed doubtful; yet when exposed to intense heat with carbonaceous matter, they form a kind of frit.

Its combination with sulphur is effected by exposing them to heat in a covered crucible: when the sulphur is in fusion, it enters into union with the lime, and forms a compound of a reddish brown colour. Its properties, like those of the other alkaline sulphurets, can scarcely be farther examined, as, when it is dissolved in water, mutual decomposition takes place, sulphuretted hydrogen is produced, and a sulphuretted hydro-sulphuret, or hydrogured sulphuret, is formed. An analogous combination is established by boiling slaked lime with half its weight of sulphur in ten times its weight of water. The liquor is of a yellow or reddish colour, according to the proportions, and has a fœtid odour. Like the other liquors of this kind, with the other alkaline bases, it absorbs oxygen speedily in its elastic form; it has in consequence been used as a eudiometrical agent, and from the state of concentration in which it can be easily obtained, it is preferred, as has already been stated, to the sulphuretted hydro-sulphuret of potash. When an acid is added to it, sulphur is precipitated, and super-sulphuretted hydrogen, or sulphuretted hydrogen, is disengaged.

Hydro-sulphuret of lime is formed by transmitting sulphuretted hydrogen gas through water in which lime is suspended: and also by exposing the solution of the sulphuret in water to the air, its excess of sulphur precipitating with a little sulphate of lime. The compound is capable, as Berthollet discovered, of crystallizing in prisms: it is soluble in water; the solution is colourless, but has a fœtid smell.

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* Journal des Mines, tom. xxxiv. p. 308.

The compound of lime with phosphorus is obtained by subliming phosphorus over dry lime, the phosphorus being placed at the bottom of a coated glass tube, with fragments of lime over it, in the proportion of 1 part of phosphorus to 8 of lime, the upper part of the tube being filled with coarse powder of lime, the orifice being lightly closed with a plug of clay, and heat being cautiously applied by charcoal, so as to raise the lime to a red heat. The greater part of the phosphorus combines with the lime, though a portion of it in vapour also escapes and takes fire at the mouth of the tube. The compound is of a dark grey or brown colour, and has a faint smell. When dropt into water, it causes an immediate production of phosphuretted hydrogen gas, which takes fire at the surface of the water.

Lime is incapable of combining with the metals; but it promotes the oxidation of several of them by water and air, and unites with their oxides. Thus, it melts with oxide of lead into a species of glass; and with oxide of iron it forms a coloured porcelain. In the humid way, it appears to combine also with both these oxides; with oxide of lead, in particular, it forms a compound, which, as Berthollet has observed, is nearly as soluble in water as lime itself, and which by evaporation may be obtained in small transparent crystals. According to the same chemist, lime-water, boiled on oxide of quicksilver, dissolves a portion of it, and forms a crystallizable compound *.

Lime combines with the acids. Its salts have some analogy in point of solubility, to those of barytes and strontites, those of the one, which are soluble, as the nitrate, muriate, and acetate, being soluble also in the others, and those which are insoluble, as the sulphate, carbonate, phosphate, and fluate, being equally so in the others. The soluble calcareous salts are distinguished by being decomposed, and the lime precipitated by potash and soda, but not by

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* Annales de Chimie, tom. i. p. 55.—61.

ammonia, the ammonia forming, as Berthollet has shewn *, a soluble ternary compound with the lime and the acid. The decomposition by potash and soda is only partial; by carbonate of potash, or soda, or even of ammonia, it is more complete, carbonate of lime being precipitated. Oxalic acid throws down lime from all the other acids, and from its compound being quite insoluble, it forms the most delicate test of its salts. The insoluble calcareous salts are decomposed by double affinity, by boiling in the solution of an alkaline carbonate.

CARBONATE OF LIME.—This is an important compound, which exists in nature in great abundance, and under a variety of forms; it is formed artificially by adding carbonic acid to lime-water, by agitating water impregnated with that acid with lime, or by decomposing any soluble salt of lime by an alkaline carbonate. But its chemical properties are generally described from those varieties of it which exist native in a state of purity.

In its neutral state, it is very sparingly soluble in water; it is precipitated on its formation; but if in small quantity, and if a large quantity of water be added, it is dissolved. It is easily dissolved by an excess of carbonic acid: hence if liquid carbonic acid be added to lime-water, a milky precipitate is at first formed; but if more of the acid be added, the liquid becomes limpid; and on leaving it exposed to the air, the excess of carbonic acid escapes, and the neutral carbonate is again precipitated. The native carbonate is often in large regular crystals, usually three or six-sided pyramids, or six-sided prisms.

When exposed to heat, carbonate of lime first loses what water it contains, and, if transparent and hard, becomes opaque and friable. If the heat be augmented, the carbonic acid is expelled, and pure lime remains. This operation is performed on a large scale, on the different varieties

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* Researches on Chemical Affinity, p. 100.

of the native carbonate, marble, chalk, and limestone, to obtain lime for the numerous uses to which it is applied. The heat is applied in a kind of open furnace or kiln, and some care is requisite that it should not be raised too high, as vitrification of the lime, by which it would be rendered incapable of slaking, is liable to occur by its combination with the argillaceous or siliceous earth which limestone contains. The same caution is requisite when the experiment is performed on a small scale in a crucible; and indeed to obtain pure lime from the carbonate, it is necessary that the decomposition by heat should be done in an iron or platina crucible. The presence of water aids the expulsion of the carbonic acid, as has been already stated, under the history of water.

The experiments of Sir James Hall have shewn, that if the separation of the carbonic acid be prevented by pressure, carbonate of lime may be fused, and by a heat comparatively moderate, intermediate between 20° and 30° of Wedgwood's scale. The result is a substance having considerable hardness and closeness of texture, and approaching by these qualities, as well as in fracture and specific gravity, to the finer kinds of limestone or marble *. Bucholz afterwards discovered, that even without compression carbonate of lime is fused. He had exposed a large quantity, 4½ lbs. of pure washed chalk, in a Hessian crucible, to a red heat, quickly raised, for an hour in a wind furnace. A thin layer on the surface, and next the sides of the crucible, was converted into lime; but this was followed almost to the centre by laminæ adhering strongly, hard and solid, half fused, and of a yellowish white colour; under this was another part extending to the bottom of the crucible, having still more decided marks of fusion; its fracture being smooth and conchoidal, and its hardness such as to cut glass; some fragments were even transparent. This fused

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* Edinburgh Philosophical Transactions, vol. vi.

chalk Bucholz found had not lost more than one *per cent.* of its acid *. The escape of the carbonic acid in such an experiment would be retarded by the access of the air (which, it has been already stated, vol. i. p. 281, favours the transition into the elastic form) being prevented, and thus the fusibility would be promoted.

Carbonate of lime is decomposed by the acids with strong effervescence, from the expulsion of the carbonic acid in the elastic state. This property of effervescing on the contact of an acid, though it may be discovered by the application of a very concentrated acid to some other salts, particularly the fluates and muriates when in powder, is much more conspicuous in the carbonates, and affords a discriminating character of carbonate of lime.

Native carbonate of lime consists, according to Kirwan, of 55 of lime, and 45 of acid; which he supposed to be also the proportion of the artificial carbonate, after exposure to heat, so as to expel its water. With this the results found by other chemists nearly correspond, the proportions assigned by Vauquelin being 56 of lime, and 43.5 of acid, by Bucholz, 56.5 and 43, by Aikin, 55.5 and 44, by Thenard, 54.34 and 43.28, by Marcet, 56.1 and 43.9, and by Berzelius, 56.4 and 43.6 †. Dr Wollaston having made the composition of carbonate of lime the basis of his scale of chemical equivalents, it was of the first importance to determine it with precision. He fixed the proportions from experiment at 56.3 of base, and 43.7 of acid. Berthollet has inferred, that this compound is a sub-carbonate, and that twice the quantity of carbonic acid would be required to form the neutral carbonate, with the same weight of lime ‡.

NITRATE OF LIME.—This salt is found in those situa-

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* Nicholson's Journal, vol. xvii. p. 250.

† Philosophical Magazine, vol. xl. p. 117.

‡ Mémoires d'Arcueil, tom. ii.

tions in which nitrate of potash is formed, and appears to derive its origin from the same process: it has also been said to be obtained from certain mineral waters; the easiest mode of obtaining it pure, is by the action of diluted nitric acid on carbonate of lime. When the solution is evaporated to the consistence of a syrup, it affords slender prismatic crystals. These are very deliquescent; and are soluble in less than an equal weight of water at 60°, and in boiling water in any proportion. They are also soluble in alkohol. Exposed to heat, they undergo the watery fusion, and the acid is soon expelled. By having been heated it becomes phosphorescent, and retains this property even when cold: it then forms what was termed by chemists Baldwin's Phosphorus. Thrown on burning fuel, it first melts, and afterwards detonates slightly. It consists, according to Kirwan, when well dried in the air, of 32 of lime, 57.44 of acid, and 10.56 of water. The real salt consists of 34.5 of base, and 65.5 of acid.

Sulphate of Lime has been long known under the names of Gypsum and Selenite, and is one of the saline substances most abundant in nature. It forms extensive strata: it is found in greater or less quantity in almost every soil: it is contained in the waters of the ocean, and in almost all river and spring water. Its presence in water is the cause of the quality termed hardness, which, independent of the peculiar taste by which it is accompanied, is known by the water being incapable of forming a solution of soap; the sulphuric acid of the sulphate attracting the alkali of the soap, and the oil forming an imperfect saponaceous compound with the lime.

Sulphate of lime is insipid, or in solution has a slight taste: it is white, and soft to the touch. It requires 500 times its weight of water for its solution at a mean temperature. At 212° it is more soluble. It is found native crystallized in lenticular crystals, or in six-sided prisms. Exposed to heat it appears to effervesce or boil, an appearance owing to the expulsion of its water. It becomes opaque, and falls into a white powder. This is what is termed Plaster, and is used in the formation of Stucco work. When water is poured on it, it absorbs it rapidly; and though as much water be added as forms a liquor of the consistence of thick cream, it soon becomes hard; hence it is easily cast into moulds, and is used for statuary, forming ornaments which are cheap, and sufficiently durable, if not exposed to humidity. When exposed to an intense heat, it seems to vitrify, but this is owing usually to the action of some other earth mixed with it, or derived from the crucible, since, when placed on a piece of pure chalk, it is infusible even by the strongest concentrated solar light. By heating it on charcoal, or by the blowpipe, it is partially decomposed, part of the oxygen of its acid being abstracted: and when exposed to the heat excited by a stream of oxygen, it is completely vitrified.

This salt is decomposed by barytes and the fixed alkalis, when boiled with them in water. It is decomposed also by double affinity, by boiling it in a solution of the alkaline carbonates. It is not decomposed by the acids. It may be dissolved by the sulphuric, but the solution is decomposed by water. The proportions of its constituent parts are, according to Kirwan, when dried at 66°, 32 of lime, 46 of acid, and 22 of water: when it has been kept ignited, 41 of lime, and 59 of acid. According to Mr J. Thomson and Berthier, calcined sulphate of lime consists of 42 of lime, and 58 of acid; and the experiments of Berthier agree with Kirwan's estimate of the water in the sulphate in its common state, amounting to 22 *per cent.* The precise composition seems to be 41.5 of base, and 58.5 of acid.

An ANHYDROUS SULPHATE OF LIME occurs in nature; it is distinguished from the common sulphate by being harder, and of greater specific gravity; its fracture is foliated, and its lustre pearly. Its composition is the same as that of the common sulphate deprived of water.

Sulphite of Lime is formed by passing sulphurous acid gas through water in which carbonate of lime is diffused: an effervescence takes place, and if, after this has ceased, the sulphurous acid gas be continued to be transmitted over the powder which remains at the bottom of the vessel, a soluble sulphite of lime is formed, which, after the liquid has been heated, is obtained crystallized in six-sided prisms acuminated by six planes. It has a taste slightly sulphureous; is efflorescent on exposure to the air, and changes very slowly into sulphate: It is less soluble than the sulphate, requiring 800 parts of water for solution, but is rendered more soluble by an excess of acid. It is decomposed by heat, a portion of sulphur being sublimed from it. It consists, according to Fourcroy and Vauquelin, of lime 47, sulphurous acid 48, water 5.

Phosphate of Lime.—Lime and phosphoric acid are capable of combining in different proportions, and from the late researches of chemists, there appears to be considerable difficulty in determining the precise combinations; nor can the determination at present be considered as certain. Berzelius, in particular, has given a series of experiments *, in which the results are very discordant, apparently from different combinations being established, which form mixtures with each other. And the difficulties are scarcely elucidated by the researches of Dulong †.

The substance which is the base of burnt bone, may perhaps be regarded as the neutral phosphate, and must probably at least be of uniform composition. It is obtained by calcining bones in an open fire, until the animal matter is entirely consumed, and the earthy residuum is per-

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* Annales de Chimie et Physique, tom. ii. p. 151.

† Mémoires d'Arcueil, tom. iii.

fectly white. The product is mixed with carbonate of lime, and small quantities of other substances: but it is obtained pure by dissolving the calcined bone in muriatic acid, and precipitating by ammonia. It is also formed by decomposing muriate of lime by phosphate of soda. It is in the form of a white powder, tasteless, nearly or entirely insoluble in water. It retains a considerable portion of water, which renders it gelatinous, and which is not easily expelled even at a red heat. Exposed to intense heat it is semi-vitrified, but not decomposed; and it is imperfectly decomposed when heated with carbonaceous matter; the strong affinity exerted by the lime counteracting the affinity of the charcoal to the oxygen of the acid. The weaker acids, as the acetic, and the dilute muriatic, nitric and sulphuric, dissolve it. From these solutions it is precipitated by ammonia, but an excess of ammonia redissolves it; by potash it is precipitated, but a portion of its acid is also abstracted from it. The alkaline carbonates precipitate it, and in excess redissolve it. The stronger acids decompose it, by abstracting partially the lime from the phosphoric acid; and if the compound of the lime with the acid employed in the decomposition be sparingly soluble, so as to be withdrawn, a soluble super-phosphate of lime is procured. The composition of the Osteo-phosphate of lime, as Dr Thomson named this compound, he stated at 100 of acid, with 79.47 of lime *. According to Berzelius, it appears to be 100, with 84.53.

When calcined bone in powder is submitted to the action of two-thirds of its weight of sulphuric acid, diluted with as much water as is sufficient to preserve a thin consistence, the greater part of the lime is abstracted by the sulphuric acid, forming sulphate of lime, and a super-phosphate of lime is dissolved, which was regarded as a distinct salt by Fourcroy and Vauquelin, who have examined its

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* Annals of Philosophy, vol. vii. p. 306.

properties*. It is very soluble in water: by evaporation of its solution, it crystallizes in silky fibres, or in brilliant scales or plates: it is liquefied by heat, and forms a transparent glass if brought into perfect fusion; the aggregation of which is such that its sour taste is much diminished, and it is permanent in the air, though slightly deliquescent in its crystallized state. This is what has been called Glacial Phosphoric Acid. When heated with carbonaceous matter, the excess of acid which it contains above that which enters into the composition of the neutral phosphate is decomposed; and by this decomposition phosphorus is obtained, according to the process which has been already described. It is doubtful whether this compound is of uniform composition. It was stated by Fourcroy and Vauquelin at 54 of acid, and 45 of lime. It has been stated by Dr Thomson at 100 of acid, with 19.86 of lime, proportions extremely different. Neither of these salts is applied to any use, except that from the superphosphate, phosphorus is usually procured; and the calcined bone ashes made into a paste with water, are used in the fabrication of assaying tests and cupels.

A compound of phosphoric acid and lime exists in the mineral kingdom, forming the minerals which have been named Phosphorite, Apatite, and Asparagus Stone; the first occurring massive, the others crystallized in equiangular six-sided prisms, usually of a green or yellowish colour, transparent, with considerable lustre. From the proportions in the composition of these minerals, they must, compared with the osteo-phosphate, constitute a sub-phosphate of lime. Klaproth found the apatite to consist of 45 of acid, with 55 of lime; the proportions assigned by Vauquelin to the asparagus stone, are 45.72, with 53.32.

Phosphite of Lime is formed by causing phosphorous acid to act on lime, until they are reciprocally saturated.

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* Mémoires de l'Institut. National, tom. ii. p. 274.

The salt is insipid and insoluble; it is not altered by exposure to the air; heated it is phosphorescent, and urged by a strong heat it melts. It consists, according to Vauquelin, of 51 of lime, 34 of acid, and 15 of water. With an excess of acid it becomes soluble, and can be obtained in small prisms.

Borate of Lime.—When this salt is formed, by adding a solution of borate of soda to lime-water, or to the solution of any of the soluble salts of lime, it is precipitated in an insoluble powder, white and insipid, the properties of which have not been more particularly examined. A borate of lime, with the addition of siliceous earth, exists native, forming the mineral which has been named Datholite.

Muriate of Lime.—When dry lime is heated in muriatic acid gas, the gas is absorbed, and muriate of lime is formed, from which water may be expelled, but the mutual action is not in this, as in the analogous experiment with barytes and strontites, accompanied with an evolution of light. When it is heated in oxymuriatic acid gas, the same salt is formed, and oxygen gas is liberated, equal to half the volume of the other. Muriate of lime is usually obtained by the action of muriatic acid on carbonate of lime, the carbonic acid being disengaged, and the muriatic acid combined with the lime. Its taste is extremely bitter, and somewhat acrid: it is very soluble in water, the water dissolving even at 32° more than its weight of the salt, and at 60°, above three times its weight, and forming a liquid, which is of a thick consistence. Its solubility is unlimited in hot water; and the solution affords crystals at a low temperature, which are regular if removed before the whole solution has by cooling and rest formed a crystalline mass: their form is a six-sided prism acuminated by six unequal planes. It is extremely deliquescent; the crystals being with difficulty dried, and quickly attracting humidity from the air: it is in consequence of this strong attraction to water, that this salt acts with so much energy on snow, liquefies with it, and by this liquefaction occasions intense cold. It is also soluble in alkohol. Exposed to heat, it suffers the watery fusion: when the heat is increased, a small portion of its acid is expelled. The residual matter is phosphorescent, and was known by the name of Homberg's Phosphorus. It is decomposed by several of the acids, which disengage the muriatic acid, and by the fixed alkalis, which precipitate the lime: and by complex affinity by the carbonates, sulphates, and phosphates. Crystallized muriate of lime consists, according to Berzelius, of lime 25.71, acid 24.69, water 49.6; the dry salt of 48.54 of acid, and 51.46 of lime. Dr Marcet gives as the composition of the real salt 49.23 of acid, and 50.77 of lime. Supposing it to be a chloride of calcium, the composition would be 36.6 of calcium, and 63.4 of chlorine.

Oxymuriate of Lime.—Oxymuriatic acid, it has been stated under its history, there is every reason to believe, combines with alkaline bases, and forms saline compounds. Of these combinations, that with lime has been principally noticed, from its having been applied as a form of employing oxymuriatic acid in the process of bleaching, an application of it which has also been considered. The analysis of oxymuriate of lime was ably executed by Mr Dalton *. The usual mode of forming it on the large scale, is to transmit oxymuriatic acid gas through slaked lime, diffused in water, or only slightly humid. In this last mode, a soft white powder is formed, nearly inodorous, which when dissolved in water, affords a bleaching liquor. This powder Mr Dalton submitted to experiment; 100 grains being agitated with 1000 of water, a portion of lime is precipitated, and the oxymuriate remains in solution. The quantity of lime which it retained was ascertained by precipitation of a given portion of it by carbonate of soda.

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* Annals of Philosophy, vol. i. p. 15, vol. ii. p. 6.

The quantity of oxymuriatic acid was determined by a method which Mr Dalton found a very delicate one, its effect in converting the green sulphate of iron into the red sulphate, a given portion of it in the gaseous state being capable of producing this change on a certain quantity of solution of the green sulphate of a determinate strength, and the solution of the oxymuriate producing the same effect, so that an equivalent quantity may be inferred. He also found the quantity directly by expelling the oxymuriatic acid gas from the solution of the salt by an acid. The composition of the powder he inferred, from the results, to be 23 of oxymuriatic acid, 38 of lime, and 39 of water. The lime which is precipitated in dissolving it in water, he considers as having been combined with the oxymuriatic acid. The powder, therefore, according to this view, is a sub-oxymuriate. When dissolved, one-half of the lime is deposited, and the solution contains an oxymuriate. The proportions of its elements are 54.7 of acid, and 45.3 of lime. When the solution is saturated by a current of oxymuriatic acid gas being sent through it, Mr Dalton infers, that a super-oxymuriate is formed, the proportions in which are 70.7 of acid, and 29.3 of lime. The dry powder formed for the purpose of bleaching, usually contains an intermixture of muriate of lime, but this is adventitious. When it is kept for some time, it suffers progressive decomposition, partly from the escape of the oxymuriatic acid gas, and partly from its conversion into muriatic acid, and a consequent formation of muriate of lime. When heated, there is a similar change, and even its solution cannot be concentrated by evaporation without decomposition.

Hyper-oxymuriate or Chlorate of Lime, it is stated by Chenevix, is deliquescent, liquefies at a moderate heat, from the influence of its water of crystallization, and is very soluble in alkohol. It produces much cold, and a sharp taste in the mouth. It is composed of 28.3 of base, 55.2 of acid, and 16.5 of water.

Fluate of Lime.—Pure fluoric acid added to a solution of lime, causes the formation of flocculi, insoluble in water, but which are soluble in an excess of fluoric acid, or in nitric or muriatic acid. The native fluate, fluor spar, occurs massive and crystallized, its crystals being cubes, often of a large size, transparent, of vitreous lustre, and distinguished by variety and beauty of colour. It is highly phosphorescent when heated; and at a high heat is fused into a perfect glass. It is composed, according to Klaproth's and Dr Thomson's analysis of it, of 32.5 of acid, and 67.5 of lime.

Siliceo-Fluate of Lime, formed by digesting the liquid siliceo-fluoric acid on lime, does not afford crystals even when evaporated to a jelly; it is insipid, and insoluble in water. Many of the varieties of fluor spar might be inferred to consist of this siliceo-fluate of lime; for when they are decomposed by an acid in metallic vessels, siliceo-fluoric acid gas is disengaged. It is more probable, however, that they consist of fluate of lime with intermixed fluate of silex. Gay Lussac and Thenard remarked, that specimens of fluor spar of this kind appear to be perfectly homogeneous; they are crystallized and transparent, are not distinguished by any obvious appearance as containing silex, and are discovered only by affording siliceo-fluoric acid *.

Hydriodate of Lime.—This salt, Gay Lussac remarks, is extremely soluble in water, and deliquescent; it melts at a heat inferior to redness. When heated in close vessels, it becomes only slightly alkaline, but if heated with the access of air or of oxygen, abundant vapours of iodine are disengaged †.

Oxiodate of Lime.—This salt is pulverulent, but may be crystallized from its solution in muriate or hydriodate of lime, which increase its solubility, in small quadrangular

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* Recherches Physico-Chimiques, tom. ii. p. 26.

† Annales de Chimie, tom. xci. p. 60.

prisms,—100 of water dissolves 0.98 of it at 212°, and 0.22 at 66°. It retains in combination about 3 *per cent.* of water. Decomposed by heat, it affords oxygen, iodine, and lime *.

The uses of lime are numerous and important. Its most valuable application perhaps is in the construction of mortar, slaked lime, with the intermixture of sand, and sometimes with other materials, forming a paste with water, superior as a cement in building to any other composition, as adhering more closely to stones, and acquiring speedily such firmess as to consolidate the mass. The lime is the ingredient on which this induration depends, and this speedily hardening, the setting, as it is called, appears to arise from the more intimate combination of the lime with the water, and the contraction, which is the consequence of this. The intermixture of the sand seems to be useful by preventing the cracking of the cement, which would follow from the contraction taking place too rapidly, and extending without interruption through a continuous mass. The more perfect induration which is gradually acquired, and which gives the requisite solidity, seems to depend partly on the more perfect combination with the water, and partly on the absorption of carbonic acid by the lime of the porous mass from the air; and accordingly the lime in mortar, after a certain time, is in the state of carbonate; and by age the induration increases, probably from the more perfect absorption, and from the vacuities being filled up by the gradual infiltration. The proportions necessary to constitute a good mortar are variable, according to the quality of the lime and of the ingredients mixed with it; one part of lime to six or seven parts of sand, the sand being of different degrees of fineness, has been stated to afford the best cement; but the proportion

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* Annales de Chimie, tom. xci. p. 84.

of sand in common use is considerably less than this: with a small proportion of lime, the ultimate induration appears to be most perfect, but when the quantity of sand is too great, the mixture has not sufficient tenacity to adhere to the stones. In old cements, Dr Irvine, who has made some observations on this subject, found the proportion of lime not to exceed one-seventh of the mass *. There is an advantage in the sand being of different degrees of fineness, as the interposition of the grosser fragments prevents the rents which occur in setting from being rectilinear, as they would be in a composition of fine sand, lime, and water alone, and the unequal contraction and multiplied fissures, probably admit better of the absorption of the air to afford carbonic acid.

Mortar which sets, and remains indurated under water, has lime also for its base, but with the addition of other substances, the rationale of the operation of which is not well understood. The puzzolane earth, or terras, a volcanic product, was used by the ancients, mixed with lime and sand, in the construction of their aqueducts, and is still employed. It consists chiefly of clay with oxide of iron. The clay iron-stone calcined is found to succeed equally well, and, added to lime, forms the base of the present water-proof cement. The power of hardening under water has been considered as depending on the calcined clay, but any apparent action that could be exerted by aluminous earth, does not account for the result. It has been ascribed with more probability to the oxide of iron, which may be supposed to form a permanent combination with the lime; and accordingly, iron filings added to cements, augment the power of resisting water. But it is affirmed, that there are limestones, which calcined, afford a mortar which sets and remains permanent in water, containing

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* Chemical Essays, p. 358.

little or no iron, and having only an intermixture of aluminous or siliceous earth; and one example of a lime-stone occurred to me corresponding to this. It is to the siliceous earth, according to Descostils, as is before stated, that the effect is owing. Oxide of manganese has been said to produce a similar result with oxide of iron. The following has been given as the analysis of the puzzolana of Italy, which added in a certain proportion to lime, forms waterproof cement,—in 100 parts, 50 of silex, 16 of oxide of iron, 25 of alumina, 3 of lime, and 6 of loss. An artificial puzzolana prepared from a calcined quartz ironstone, which was found to be even superior to the other, was found to consist of 50 of silex, 31 of oxide of iron, 16 of alumina, and 3 of oxide of manganese and loss *. The composition which forms the best cement under water, is not precisely that which remains most permanent in the air, some variations in the proportions at least being best adapted to each.

In the practice of agriculture, advantage is derived from lime as a manure; and though part of its utility may depend on its mechanical operation on the soil, and part on its chemical agency in promoting the decomposition of vegetable and animal substances, the whole theory of its action is not perhaps perfectly understood. In practical chemistry, and in many of the chemical arts, it admits of numerous applications, from its chemical agencies, and in particular, from its relations to the acids, the compound salts, the other earths, and many of the vegetable and animal products. In medicine, it is employed as an antacid and astringent.

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* Nicholson's Journal, vol. xii. p. 337.

CHAP. IV.

OF MAGNESIA AND ITS BASE.

HOFFMAN first distinguished this earth as different from the others. It had been employed in medicine, but had been supposed to differ little from carbonate of lime. Hoffman observed, that it forms with sulphuric acid à salt different from that formed by lime with the same acid. Margraaf confirmed this. Dr Black soon afterwards undertook the investigation of its properties. He established clearly the distinction between it and lime, and shewed that it has properties different from all the other earths. Its chemical relations were farther investigated by Bergman. It is an ingredient in many fossils; and several of its salts are found in mineral springs, and in the water of the ocean. It is from these saline combinations that it is obtained, by an artificial process.

The sulphate of magnesia is used for this purpose. One part of it is dissolved in 20 of water, and the solution is filtered: there is added to it, while hot, a solution of potash, or soda, as long as any precipitation is produced: the alkali combines with the sulphuric acid, the magnesia is separated, its depôsition being facilitated by boiling the liquor slightly: it is washed with water, and is dried by a moderate heat. Or, what is a preferable mode, as abstracting more perfectly the sulphuric acid, the carbonate of potash or soda is used for the precipitation; the carbonate of magnesia is thus obtained: and from this the carbonic acid is expelled, by exposing it to a red heat.

Magnesia, submitted to the action of galvanism, is less acted on than the preceding earths, probably from its insolubility and the difficulty therefore of rendering it a conductor of electricity. But by submitting to experiment some of its saline compounds, as the sulphate or nitrate in contact with mercury, the decomposition seems to be effected, and an amalgam obtained; magnesia being reproduced in the experiments of Davy, when the metallic matter was exposed to the air. He did not succeed in expelling the quicksilver from the magnesian base, the glass of the tube being acted on before this result was obtained. In an experiment in which the process was stopt before the mercury was entirely driven off, a solid was obtained, having the same whiteness and lustre as the other metals of the earths. "It sunk rapidly in water, though surrounded by globules of gas, producing magnesia, and quickly changed in air, becoming covered with a white crust, and falling into a fine powder, which proved to be magnesia." He afterwards, by passing potassium over magnesia at a high temperature, and introducing quicksilver into the tube while hot, obtained an amalgam, which was deprived of its potassium by the action of water. It then appeared as a solid white metallic mass, which by exposure to the air became covered with a dry white powder, and when acted on by weak muriatic acid gave off hydrogen gas in considerable quantities, and produced a solution of magnesia*. The metallic base he proposed to name MAGNIUM. Magnesium denotes better its relation to the earth.

On the principle already illustrated, in assigning the proportions of the elements of the other earths, those of magnesia may be determined: 100 of real sulphuric acid saturate a portion of base containing 20 of oxygen; it saturates in this quantity 49.3 of magnesia; hence 100 of magnesia are composed of 40 of oxygen, and 60 of magnesium.

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* Philosophical Transactions, 1808, 1810.

MAGNESIA exists under the form of a white, light powder, soft to the touch, inodorous, and impressing a slightly bitterish taste. Its specific gravity is about 2.3. It changes the more delicate blue vegetable colours to a green.

When pure, it is infusible when exposed even to the most intense heats. In the focus of the most powerful burning mirror, or in the heat excited by a stream of oxygen gas directed on burning charcoal, it is not melted; and even in the more intense heat excited by the kindled stream of oxygen and hydrogen gases, its fusion is doubtful; Mr Hare having obtained only small black vitreous masses when it was exposed to the flame on charcoal, and the fusion being probably promoted by some of the substances contained in the charcoal. Mr Children found it to be only agglutinated by the intense heat of his powerful galvanic battery. Dr Clarke succeeded in producing vitrification, both of pure magnesia and its native hydrate, before the flame of hydrogen and oxygen gases, but with more difficulty than almost any other body. When magnesia is made into a paste with water, it contracts when exposed to a sudden heat as alumina does, but not to the same extent.

This earth may be said to be nearly insoluble in water; one part of it requiring for its solution, according to Kirwan's estimate, not less than 7900 times its weight; Mr Dalton found 16,000 necessary. When dry, it absorbs its weight of water, but it does not form an adhesive paste, or at least one very slightly so. When precipitated from any of its saline solutions by an alkali, it retains a kind of gelatinous consistence in drying, and a degree of firmness when dried. In this state it appears to retain water in weak combination. The proportion is estimated by Davy at nearly a fourth of its weight. A native hydrate exists as a mineral production, in masses of a foliated texture, white, and in thin plates transparent: this is composed of 70 of magnesia, and 30 of water.

Magnesia and the alkalis exert no mutual action; nor does it appear to act with much energy on the other earths. With barytes or strontites it does not combine. It exerts no sensible attraction to lime but at an intense heat; they combine by fusion at 150° or 160° of Wedgewood, when the lime is in larger proportion than the magnesia; in equal parts, they do not melt at these heats. It exerts an attraction to alumina in the humid way, which appears to be one of the strongest that one earth has to another, as is displayed in a singular fact, observed by Chenevix in the analysis of some magnesian fossils, that although magnesia cannot be precipitated entirely from any of its salts by ammonia, yet, if alumina be present, its precipitation is complete. It does not melt, however, with alumina alone at the most intense heat. Ternary mixtures of magnesia, lime, and silex, magnesia, lime, and alumina, and magnesia, alumina, and silex, are more fusible, forming in various proportions a porcelain, or glass, though in all these magnesia must be in a proportion inferior to that of the other earths, to admit of the fusion of the mixture *.

No chemical action appears to be exerted between magnesia and the simple gases, nor between it and any of the simple inflammables, sulphur excepted. They combine, though not very intimately, when the sulphur is in fusion, or when it is boiled with the magnesia in water. Sulphuretted hydrogen transmitted through water, in which magnesia is suspended, dissolves a small quantity of it; but the properties of the hydro-sulphuret have not been examined. The Sulphuretted Hydro-sulphuret is a combination which appears to be imperfectly established; a liquor having only a faint yellow colour, and a slightly fœtid smell, being formed, when magnesia and sulphur are boiled together in water, or when they are exposed to heat in a crucible, and afterwards dissolved in water.

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* Kirwan's Mineralogy, p. 62. &c.

Magnesia has no action on the metals, nor does it appear even to combine by vitrification with the metallic oxides.

Magnesia combines with facility with the acids. Its salts are in general very soluble in water; they are crystallizable, and have a bitter taste. Its attractions to the acids have been supposed to be inferior to the attractions of the fixed alkalis, of lime, barytes, and strontites, as its salts are decomposed by them: but these decompositions are only partial, and are in part owing to the influence of the force of cohesion. From the tendency of ammonia to form ternary saline compounds, they are also decomposed partially by its action, a portion of the earth being precipitated, while the remainder enters with the ammonia and the acid of the salt into ternary combination, constituting what have been named Ammoniaco-magnesian Salts. The carbonates of potash and soda produce more perfect decomposition; but what is a very characteristic property of the magnesian salts, though they are decomposed by sub-carbonate of ammonia, the carbonate, or what is named the bi-carbonate, gives rise to no apparent decomposition; when it is added to their solutions, the magnesia is not precipitated, but remains in solution, without the transparency being impaired. If after this addition, however, a solution of phosphate of soda be dropt into the liquor, a copious precipitate is thrown down, of a white colour, with considerable lustre; this is the triple phosphate of magnesia and ammonia, the least soluble of the magnesian compounds, and the production of which, therefore, forms their most delicate and accurate test. The direct addition of sub-phosphate of ammonia to the solution of a magnesian salt, produces the same effect.

Carbonate of Magnesia is a compound of some importance from its medicinal use. It is prepared according to the directions given in the Pharmacopœia, by mixing equal weights of sulphate of magnesia and sub-carbonate of potash dissolved separately in twice their weight of water, and diluting the mixture immediately with 8 parts of warm water: the magnesia attracts the carbonic acid; and the compound is precipitated, while the sulphate of potash that is formed remains in solution. The mixture is made to boil for a few minutes; it is poured upon a cloth, on which the precipitate of magnesia remains, and is washed with water till it is tasteless.

On a large scale the process is conducted somewhat differently. Instead of the sulphate of magnesia, the bittern, or liquor remaining after the crystallization of sea-salt, is used. It is precipitated either by carbonate of potash, or by an imperfectly saturated carbonate of ammonia. The bittern is heated to the boiling point: the alkaline solution is added, and the fire is immediately withdrawn. The mixture is stirred, to promote the decomposition. It is then poured on canvas, stretched over a cistern: the liquor, holding the muriate and sulphate of potash, or ammonia, strains through: the carbonate of magnesia remaining on the cloth is washed with water till it is tasteless. When the washing is completed, a frame of wood, divided into small squares, is placed upon the thin paste, so as to divide the magnesia. After it has become firm, the drying of it is completed, by placing it in a stove, or over heated flues. The success of the process, so as to obtain the product light, smooth, white, and tasteless, is considerably dependent on the purity of the alkali, the mode of precipitation and washing, and the purity and softness of the water with which it is washed.

Carbonate of magnesia is perfectly white, nearly, if not entirely tasteless when pure, possessing little coherence, and of a specific gravity not more than 2.3. It is very sparingly soluble in water; requiring at least 2000 times its weight at the temperature of 60° for its solution. It is decomposed by a red heat, and its carbonic acid expelled. Mr Dalton found, that 100 grains of it well dried, lost 40 *per cent.* from the disengagement of carbonic acid by the action of acids, and 57 *per cent.* by exposure to a red heat. The difference between these gives of course the quantity of water; and hence 100 parts are composed of 43 of magnesia, 40 of carbonic acid, and 17 of water [*]. The proportions, however, vary considerably, according to the mode of conducting the process. Kirwan states them at 45 of magnesia, 34 of acid, and 21 of water. In all these proportions it appears to be a sub-carbonate, as is evident from its being formed by double decomposition of a magnesian salt by an alkaline sub-carbonate, and by a large quantity of carbonic acid being disengaged with effervescence, when it is formed in this manner by a carbonate approaching more nearly to neutralization.

The compound analogous to the Carbonate is formed, according to Fourcroy, when the powder of the sub-carbonate is diffused in water, and carbonic acid gas is transmitted through it: a portion is dissolved; and when the solution is allowed to evaporate spontaneously, small hexagonal prismatic crystals are formed. They are transparent, but efflorescent; they dissolve in 48 parts of water at 60, and by slow evaporation the solution again affords crystals. They consist of 25 of magnesia, 50 of acid, and 25 of water. If these proportions are correct, they must constitute a super-carbonate. A similar compound is said to be obtained, when solutions of sulphate of magnesia and carbonate of potash mixed, are allowed to remain at rest; crystals being deposited after two or three days. A product obtained in crystalline grains, in this mode, was found by Mr Dalton to be the sub-carbonate, with an additional portion of water. In rhomb spar, the carbonate exists, composed of 47 of magnesia, and 53 of carbonic acid.

Nitrate of Magnesia. This salt is found, with the nitrates of lime and potash, in the materials of nitre beds, and is contained in the lixivium they afford. To have it pure, it is prepared by the combination of its principles.

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[*] Chemical Philosophy, p. 514.

Its taste is bitter and acrid. Its crystallization is scarcely regular, but exhibits a mass of small needles: by spontaneous evaporation, it concretes in quadrangular prisms: it is deliquescent; is soluble in its weight of water, at a mean temperature, and in half its weight of boiling water: it is also soluble in alkohol. By exposure to heat, it is decomposed: its acid being partly expelled, partly resolved into its constituent principles. It consists, according to Kirwan, of 22 of magnesia, 46 of acid, and 22 of water.

Sulphate of Magnesia. This salt is found in sea-water, and in many mineral waters. The mineral springs of Epsom afforded it in large quantity; hence the origin of the name of Epsom or English salt. At present it is chiefly extracted from sea-water. It remains with a portion of muriate of magnesia, dissolved in the liquor after the crystallization of the sea-salt. This brine, or Bittern as it is termed, is boiled down until it afford the sulphate of magnesia, on cooling, in acicular crystals; sometimes sulphuric acid or sulphate of iron is added, which decomposes the muriate of magnesia, and increases the quantity of sulphate. It is also prepared from the action of sulphuric acid on magnesian lime-stone.

The salt, as it is usually met with, exhibits a mass of needle-like crystals, which are deliquescent; but this deliquescence is owing to the admixture of muriate of magnesia, as the pure sulphate is rather efflorescent. By a second solution and crystallization, it is in a great measure freed from this; and by slow evaporation of its solution, it crystallizes in quadrangular prisms acuminated by four planes. These are soluble in little more than their weight of water, at 60°, and in three-fourths of their weight of boiling water. They undergo the watery fusion at a moderate heat, and lose their water of crystallization. The dry mass which remains is melted in a strong heat, but is not decomposed. One hundred parts of crystallized sulphate of magnesia, according to Kirwan, consist of 29.35

parts of acid, 17 of earth, and 53.65 of water: according to Henry, of 37 of acid, 19 of magnesia, and water 44. In this latter estimate, however, the proportion of water of crystallization is too low. Dr Henry has since found, that 100 of the salt dried at a low red heat are composed of 67 of acid, and 33 of magnesia; and supposing the crystallized salt to contain 0.50 of water of crystallization, which is nearly the average of different results, its composition will be 33.5 of acid, and 16.5 of base, with 50 of water. Berzelius states the composition of the dry salt at 66.6 of acid, and 33.4 of base.

SULPHATE OF MAGNESIA AND SODA.—In the process of purifying the sulphate of magnesia which is obtained by evaporation from the bittern of sea-water, a salt sometimes crystallizes, which is possessed of peculiar properties. On submitting it to analysis, I found it to be a triple compound of sulphuric acid with magnesia and soda. The salts which adhere to the sulphate of magnesia at the first evaporation, are muriates of magnesia and of soda, and probably also a little sulphate of soda. To remove these it is dissolved in water, and by evaporation is again crystallized; a fresh quantity is added to the residual liquor, and by farther evaporation a new crystallization is produced; this is repeated for a third or fourth time; and it is in these latter crystallizations that the triple salt is formed, frequently in such quantity as to be precipitated even in the boiler. It crystallizes in rhombs, at first irregular and semi-transparent; but by a second crystallization is obtained in more regular rhombs, truncated on the angles and edges, and transparent. The crystals are permanent in the air; they dissolve in little more than thrice their weight of water at 60°, and they do not undergo the watery fusion, but decrepitate from heat, properties in which this salt differs entirely from sulphate of magnesia or of soda: its taste too is less bitter than that of either of these salts. I found it to consist, in 100 parts, of sulphate of magnesia 32, sulphate of soda 39, water of crystallization 28, or admitting a little loss to be water, 29[*]. It is not formed, I found, by the direct combination of these two salts. In the process in which it is obtained, its production, from the information I have received from an intelligent manufacturer, appears to depend on the mutual action of sulphate of magnesia and muriate of soda, the triple salt forming from the combination of its acid with the two bases, and equivalent portions of the two muriates of soda and magnesia being at the same time produced. Its formation depends much on the proportions in the saline liquor; the object of the manufacturer is to prevent its production, and when it begins to form, the effect may be prevented by altering the proportions by the addition of a portion of muriate of magnesia. It may be employed with peculiar advantage as a purgative salt; it is not improbable even that it exists as a triple salt in some of the purgative mineral waters, and it might therefore, with a certain degree of dilution, be employed as a substitute for them. From some observations by Mr Heales[†], it appears not to have been altogether unnoticed, though it had not been particularly examined or submitted to analysis.

SULPHATE OF MAGNESIA AND AMMONIA.—Fourcroy describes this salt as formed by adding ammonia to a solution of sulphate of magnesia; a partial precipitation of magnesia takes place, and the liquor by evaporation affords crystals of the triple compound: it is also formed on mixing solutions of sulphate of magnesia and sulphate of ammonia. The crystals are octohedrons, less soluble in water than either of the binary salts; they suffer the watery fusion, and by a strong heat undergo decomposition. It is composed of 32 of sulphate of ammonia, and 68 sulphate of magnesia.

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[*] Transactions of the Royal Society of Edinburgh, vol. viii. p. 294.

[†] Philosophical Magazine, vol. xlviii. p. 142.

Sulphite of Magnesia is formed, by passing sulphurous acid through water in which magnesia is diffused. It is at first a powder, which is gradually dissolved; and by exposure to the air, crystals form, which are flattened tetraedrons. Its taste is sweetish, and earthy: it is inodorous; is soluble in 20 parts of cold water, and in less boiling water. It gradually passes into sulphate of magnesia, by exposure to the air. It consists of 16 magnesia, 39 sulphurous acid, and 45 of water.

Phosphate of Magnesia.—This compound is formed by the solution of the earth in the acid; or it may be obtained more distinctly crystallized, by a process given by Fourcroy:—mixing equal parts of the solutions of sulphate of magnesia and of phosphate of soda; in a few hours crystals of phosphate of magnesia form. They are compressed prisms: they effloresce speedily on exposure to the air; require at least 50 parts of cold water for their solution, but dissolve more abundantly in boiling water, so that the solution affords crystals on cooling. They lose their water of crystallization when exposed to heat, and by a stronger heat are melted into a glass.

Phosphate of Magnesia and Ammonia.—This triple compound is formed very readily, when to a solution of a magnesian salt, carbonate of ammonia is added, and phosphate of soda is dropt in; or when sub-phosphate of ammonia is added, preserving in either case an excess of ammonia in the liquor. It forms a copious precipitate, light and smooth, somewhat scaly in appearance, extremely white, with a pearly lustre, and peculiarly distinguished by the facility with which, when stirred with a rod, it forms streaks on the sides of the vessel. It is insoluble, or nearly so, in water: but it dissolves easily in weak or dilute acids: it retains a portion of water, which is expelled at the heat of 100; in this state it contains 0.19 of magnesia: by exposure to a red heat the ammonia is disengaged, and phosphate of magnesia remains, containing in 100 parts

40 of magnesia. This triple compound is not unfrequently a product of the animal system; it is more particularly a frequent ingredient of urinary concretions, and exists also in the urine.

Phosphite of Magnesia is produced on adding a solution of an alkaline phosphite to a solution of sulphate of magnesia, appearing gradually in the form of a white flocculent precipitate. It is insipid, and so sparingly soluble, as to require 400 parts of water for its solution. Its solution suffers an imperfect crystallization. When heated, it is phosphorescent, and melts. It consists, according to Vauquelin, of 20 of magnesia, 44 of acid, and 36 of water.

Borate of Magnesia.—The earth is dissolved by the liquid boracic acid, and the solution, on evaporation, affords a crystalline matter, of no regular form. It is also formed by adding the solution of borax to a soluble magnesian salt; the borate of magnesia being precipitated in the state of an insoluble and insipid precipitate. It is fused without decomposition by heat. The compound of it, with a portion of lime, forms the mineral named Boracite, to be afterwards noticed. The lime, according to Vauquelin, is not essential to the composition; it is therefore a native borate of magnesia. It is crystallized in cubes, truncated on their edges and angles, more or less transparent; hard, so as to scratch glass; insoluble in water; fusible at a high heat; and distinguished by becoming electrical at a lower heat, the angles which are truncated becoming positive, and the others negative.

Muriate of Magnesia.—This salt is that which, next to muriate of soda, is contained in largest quantity in sea-water. As it is difficultly crystallizable, it remains after the sea-salt has been crystallized, and forms the principal constituent part of the bittern; by boiling this down to a very concentrated solution, the muriate at a low temperature is obtained in a mass of needle-like crystals. It is likewise found in salt springs, and in mineral waters. It has a very bitter nauseous taste. It is very soluble in water, and its crystals deliquesce, and require little more than half their weight of water for solution. It is soluble in alkohol, and communicates to it the property of burning with a yellow or reddish flame. Exposed to a strong heat, it is decomposed, its acid being driven off. It consists, when dry, of 31.07 of magnesia, 34.59 of acid, and 34.34 of water. Its composition had not been determined in its crystallized state. I found it to be 21.3 of magnesia, 29.4 of acid, and 49.3 of water.

OXYMURIATE OF MAGNESIA.—Magnesia appears to be capable of combining directly with oxymuriatic acid, nearly in the same manner as lime; and of forming an analogous compound, in which, while the suffocating odour of the oxymuriatic gas is removed, the power of affecting the vegetable colours remains. The compound has been formed in a similar manner,—passing a current of oxymuriatic gas through water in which magnesia is suspended, or even through the powder of magnesia. This oxymuriate has been applied to a particular case in bleaching, that of cloth for calico-printing, in which the cloth is afterwards to be impressed with a coloured design. When the common bleaching liquor, prepared from oxymuriate of lime, is employed for this purpose, a minute quantity of the lime appears to remain on the fibre of the cloth, and in the last operation, that of clearing by immersion in water acidulated with sulphuric acid, sulphate of lime is formed; which, when the cloth is dyed, affects the colours as a mordant, and alters their shades. Oxymuriate of magnesia has not this disadvantage, as, if any minute portion of it remain in the cloth, the sulphuric acid forms sulphate of magnesia, which is so soluble that it is easily removed in the washing. This improvement was introduced by Mr Ramsay *. The expence of the magnesia presents the

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* Philosophical Magazine, vol. xl. p. 226.

only difficulty in employing it. Mr Wilson has suggested a method of preparing the liquor, by which this may be partly obviated,—decomposing oxymuriate of lime, prepared in the usual method, by sulphate of magnesia. He finds, that in mixing solutions of them a double decomposition takes place, the lime combining with the sulphuric acid, and forming the sulphate which is precipitated, while the magnesia combines with the oxymuriatic acid, and remains in solution [*]. This process must also afford the oxymuriate of magnesia in its purest form, and of definite composition. Its properties have not been farther examined, and there must probably be the same difficulty of obtaining it in any other state than that of solution, as there is with regard to oxymuriate of lime.

HYPER-OXYMURIATE OR CHLORATE OF MAGNESIA.—This salt may be obtained by the general process employed by Chenevix for the preparation of the earthy hyper-oxymuriates. He merely remarks with regard to it, that it is similar in its general properties to that of lime; and that it consists of 25.7 of base, 60 of acid, and 14.3 of water.

FLUATE OF MAGNESIA.—When carbonate of magnesia is heated gently with pure fluoric acid in a silver bason, there is a brisk effervescence, and a fluate is formed pulverulent, insipid, not decomposed by heat, insoluble in water, and nearly insoluble in acids. Fluate of magnesia is also formed on mixing solutions of fluate of potash, and sulphate of magnesia; a jelly consolidates which is soluble in acids; when this is dried, it acquires the properties of that directly formed. The liquid siliceo-fluoric acid dissolves magnesia, and forms a gelatinous solution, which is probably a Siliceo-fluate of Magnesia.

HYDRIODATE OF MAGNESIA.—Gay Lussac states this salt to be deliquescent, and difficultly crystallizable. On heating it to redness without the admission of air, the mag-

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[*] Annals of Philosophy, vol. viii. p. 127.

nesia allows the acid to escape*. The OXIODATE does not appear to have been examined.

Magnesia is scarcely applied to any use, except that in its pure form, and in several of its saline combinations, it is employed in the practice of medicine; and some of the native compounds of it with other earths are used sometimes in the manufacture of porcelain.

CHAP. V.

OF ALUMINA OR ARGIL.

THIS earth exists nearly pure in some of the gems; but in these fossils the aggregation is so great, that its chemical relations can scarcely be discovered. It is therefore obtained by an artificial process. The salt, known by the name of Alum, contains it in combination with sulphuric acid, and a portion of potash: one part of this salt is dissolved in 20 parts of water, and the solution being filtered; liquid ammonia is added as long as any precipitation is produced. The precipitate is well washed, and, when dried, has been supposed to be the pure earth. It retains, however, a little sulphuric acid combined with it: to obtain it pure, therefore, it ought to be re-dissolved in nitric acid, the sulphuric acid abstracted by nitrate of barytes, and the earth again precipitated by ammonia; it is to be well washed, and, when dried, exposed to a low red heat. There are some varieties of the alum of commerce composed of alumina with ammonia and sulphuric acid; and from these the pure earth may be obtained by exposure to

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* Annales de Chimie, tom. xci. p. 65.

a red heat, the acid and ammonia being expelled, a method which Gay Lussac has pointed out as the easiest by which it can be procured *. In this country, however, these varieties of alum are scarcely met with. The existence of this earth as a principal constituent part of the natural clays, was first shewn by Geoffroy and Hellot; and its properties were determined by Margraaf. From existing as the basis of clay, it derives the name of Argil. It is named Alumina, as being the base of the aluminous salts; and this last name is now generally adopted.

Davy endeavoured to decompose this earth, but the methods which had usually proved successful failed. That which succeeded best, consisted in submitting it to galvanic action in fusion with potash, or soda, metallic globules being produced, consisting principally of the alkaline base; but which also afforded when oxidated traces of the earth, along with the re-production of alkali. Similar imperfect results were obtained by the action of potassium alone, or with mercury, on alumina. By exposing the earth heated to whiteness to the vapour of potassium, potash is formed, indicating the oxygenation of the potassium, and in the mass small particles of a grey colour and metallic lustre are found, which become white when heated in the air, and slowly effervesce in water. Berzelius has inferred, from the quantity of acid which alumina saturates, on the principle already stated under the history of the other earths, that it is composed of 47 of oxygen, and 53 of metallic base †.

ALUMINA, obtained by the process above described, is in the form of a light white powder, spongy, and adhering when applied to the tongue: it is tasteless; is smooth to the touch: it imbibes water, and, when kneaded with it,

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* Annales de Chimie et Physique, tom. v. p. 101.

† Annales de Chimie, tom. lxxxii.

forms an adhesive plastic mass, and it is from this earth that the natural clays derive their plastic quality. It may be easily diffused through water, but is quite insoluble in it. It appears, however, to form a combination with it. T. Saussure remarked *, that the precipitate thrown down by an alkali from a solution of alum, is different in its appearance according to the quantity of water with which the solution had been diluted. If it were concentrated, the precipitate, when dry, is a light friable powder, which adheres to the tongue, while, if dilute, the precipitate dried is transparent, yellow and brittle, does not occupy so much volume, and does not adhere to the tongue. The former he names *spongy*, the latter *gelatinous* alumine; from both a considerable portion of water is expelled by heat; the latter he found to retain the water contained in it more forcibly than the other. After incandescence it still contains 0.15 of water; alumina appears therefore to have an affinity to water: and in its usual state is a hydrate. It occurs also in nature combined with water.

The paste, formed by kneading this earth with water, contracts when exposed to heat, and this even after all the water has been expelled from it. The circumstances connected with this contraction, and its application to pyrometry, have been already considered, (vol. i. p. 226, 259.). The clay thus heated loses its plastic power, and acquires greater hardness, so as to be capable of scratching glass, and of striking fire with steel.

In the intense heat of the most powerful burning mirror, alumina is not fused. Lavoisier, however, and Guyton, found it to be melted by the heat excited by a stream of oxygen gas directed on burning charcoal: it formed a white semi-transparent enamel of great hardness †.

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* Journal de Physique, tom. lii.

† Journal de l'Ecole Polytech. Cah. III. p. 299.

No chemical action is exerted between alumina and oxygen, nitrogen, or hydrogen.

Alumina has the property of combining, in the humid way, with the fixed alkalis. When any of its salts is decomposed by potash or soda, if an excess of alkali be added, the precipitate first formed is re-dissolved; a solution of the pure earth is also effected, when it is boiled in an alkaline solution. It appears, that the combination may also be effected in the dry way; for, although the mixture of it and either of the fixed alkalis is not fused into a perfect glass, yet a species of frit is formed, and the earth is rendered soluble in water. This combination of alumina with an alkali is subverted, by the addition of an acid, which saturates the alkali, and precipitates the earth. If ammonia dissolve alumina, it is in very minute quantity. Carbonate of ammonia dissolves no sensible portion of it *.

Alumina exerts affinities to other earths, and of any of the bodies belonging to this class, it appears to do so with most force. It unites with lime, barytes, strontites, magnesia, and silica, both in the humid and the dry way. Barytes, it has been already remarked, communicates solubility to it, so that, when equal parts of these earths are boiled in water, both are dissolved; it was stated by Vauquelin, that barytes, by its affinity to alumina, abstracts it from its acid solutions, a precipitate being formed, when barytic water is added to a solution of muriate of alumina, which consists of the two earths combined. According to Darracq and Chenevix, however, this precipitation does not take place. Strontites has an effect on alumina similar to that of barytes: five parts of it boiled with one render a part of it soluble, while a portion of the strontites remains insoluble in combination with another part of the alumina. Lime has also an attraction to this earth. When added to lime-water, it attracts the lime, as Scheele observed, and

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* Vauquelin, Annales D'Histoire Naturelle, tom. xv. p. 15.

an insoluble combination of the two earths is established. Chenevix remarked, that when a solution of potash is boiled on a mixture of lime and argillaceous earth, the latter is dissolved, together with a greater portion of lime than can be attributed to the dissolving power of the water alone; while, if the alkaline solution be boiled on lime alone, no more lime is dissolved than would be by the water of the solution, a proof that its solubility is promoted by the other *. These earths also combine, though with difficulty, at very intense heats. They cannot be fused in a furnace; but when the alumina predominates, they are melted by the heat excited by oxygen gas. With magnesia it does not unite readily. A mixture of equal weights of these two earths, Guyton found to remain pulverulent at a heat at which the crucible began to vitrify; and Kirwan found, that in whatever proportion they were mixed, they exerted no mutual action at the most intense heat. The affinity, however, between alumina and magnesia in the humid way, is shewn in the fact already noticed, of magnesia not being precipitated entirely from any of its solutions by ammonia, while, if alumina be present, its precipitation is complete. Thus Chenevix found, that on adding an excess of ammonia to a solution of muriate of magnesia, mixed with a large proportion of muriate of alumina, nothing remained in solution but muriate of ammonia: the two earths being precipitated in combination, and their mutual affinity was even sufficient to resist the action which potash exerts on aluminous earth †. The exertion of a mutual attraction between silex and alumina, in the humid way, is shewn, in the experiment of Guyton already quoted; in which, when a solution of silicated potash, and of alumina and potash, are mixed, the two earths are precipitated in combination, by which the properties of each

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* Philosophical Transactions, 1802, p. 346.

† Ibid. p. 345.

are modified. The same affinity is exerted in the dry way: when favoured by a very intense heat, they enter into fusion, and form a milky glass or enamel.

This combination of siliceous and argillaceous earths is the basis of Porcelain, and, with the addition of various proportions of other earths, forms the different varieties of pottery, from the finest porcelain to the coarsest earthen ware.

Though siliceous earth is the ingredient in largest proportion in these compounds, yet it is the argillaceous which gives them their characters, as it communicates ductility to the mixture when soft, and renders it capable of being turned into any shape on the lathe, and of being baked. The clays are native mixtures of these earths; but they are often unfit for the manufacture of the finer kinds of porcelain, from other ingredients which they contain: lime is usually present; when it is not in larger proportion than 5 or 6 parts in 100, it does not injure the quality of the porcelain; but in a larger proportion, it renders the mixture too fusible: oxide of iron, when in any perceptible quantity, communicates a yellowish or red tinge.

The perfection of porcelain, therefore, depends greatly on the purity of the earths; and hence the purest natural clays, or those consisting of silica and alumina alone, are selected. Two substances have been brought to Europe, as the materials from which the Chinese porcelain is formed,—what have been named Kaolin and Petuntse. The kaolin, according to Vauquelin's analysis, consists of silex 74, alumina 16.5, lime 2, and water 7; the petuntse, of silex 74, alumina 14.5, lime 5.5: the two, when mixed, therefore, consist of argillaceous and siliceous earths, with less than 5 *per cent.* of lime. It is difficult to procure, in Europe, natural clays equally pure, and hence, in part, the difficulty of imitating the porcelain of the East; such clays, however, have now been discovered in different countries, and the European porcelain has attained considerable perfection. The fine Dresden porcelain, that of Berlin, the French porcelain, and the finer kinds which are formed in this country, are manufactured of the clay which has received the name of Porcelain Earth, and which appears, in general, to be derived from the decomposition of the feldspar of granite. The clay of Cornwall, from which the finer kinds of English Porcelain is made, has this origin *. Earthy mixtures, containing magnesia, are also used in the manufacture. Giobert analysed an earth, which had long been employed for this purpose, and considered as a clay of great purity, and found that it consisted almost entirely of carbonate of magnesia and silex †.

The proportion of the earths to each other is likewise of importance; and from differences in this respect arises the necessity frequently of employing mixtures of clays. The proportion of silex in porcelain of a good quality is, according to Vauquelin, at least two-thirds of the composition; and of alumina, from a fifth to a third: magnesia is of utility, by lessening the tendency which the composition of the other earths alone has to contract in baking. From what we know of the fusibility of mixtures of these earths, too large a proportion of magnesia will render the composition too fusible.

In the manufacture of the finer kinds of porcelain, the ingredients are carefully washed, dried, and ground to a very fine powder, which is passed through a sieve. This is made into a paste with water, which is well kneaded, so as to be uniform in composition, or, to avoid the labour of this, it is diffused in water, so as to form a liquid of the consistence of cream, from which the superfluous water is dissipated. The vessels shaped from this paste are baked in earthen pots, to render them tolerably hard and compact: they are then covered with the materials for glazing,

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* Annals of Philosophy, vol. iii. p. 180.

† Nicholson's Journal, vol. xii. p. 277.

which, in the better kinds of porcelain, consist of a mixture of earths which form a compound more vitrifiable than the porcelain itself. These materials are diffused in fine powder in water, the baked vessels are dipt in this, the surface is thus covered with a thin crust, the water being absorbed. When dry, they are placed in the earthen pots or seggars, and exposed to a very intense heat. The solid matter of the porcelain undergoes a semi-vitrification, whence it possesses all the closeness of glass, and has an additional value in being less brittle, and more able to bear sudden alterations of temperature: it derives also much beauty from its semi-transparency and white colour. The glazing on the surface is, from its greater fusibility, more completely vitrified, and therefore more smooth and impervious.

With regard to the theory of the kind of vitrification which constitutes porcelain, Reaumur, who first investigated this subject, supposed, that part of the matter is completely vitrified by the heat, and is thus in the state of a glass; while another part has remained infusible, is diffused through this, diminishes its transparency, and gives it whiteness and semi-transparency. In the coarser kinds of porcelain, the heat applied, he supposes to have been such as to have produced merely semi-vitrification, whence the substance remains opaque, but may be completely vitrified by a stronger heat. This last opinion is probably the just one with regard to every variety of porcelain; and even if the fusion were complete, it would not follow that the product must be a transparent glass.

Mr Wedgwood ascertained the fusibility of the principal porcelains. Several kinds manufactured in England underwent perfect vitrification, at temperatures from 90° of his scale to 120°. One kind, manufactured at Bristol, shewed no appearance of vitrification at 135°. The common Chinese porcelain did not vitrify completely by any heat, but began to soften at 120°, and, at 156°, became so soft as to lose its shape. The real Nankeen porcelain did not soften in any heat that could be applied: its internal substance even remained of its granular texture. The Dresden porcelain was more refractory than the common Chinese, but less so than the Nankeen.

The inferior kinds of porcelain, or pottery, are prepared by the same process as that just described: less pure, but more fusible materials being employed, and a less degree of heat being applied. The better kinds of English stoneware are composed of pipe-clay, and pounded flint. The yellow stoneware is made of the same materials, in other proportions. The first is glazed, by throwing sea-salt into the furnace in which it is baked; the salt is converted into vapour, and this being applied to the surface of the stoneware, vitrifies it, and forms an excellent glazing. The yellow stoneware is glazed, by dipping the baked ware in water, in which is suspended a mixture of pounded flint, glass, and oxide of lead. In the glazing of some kinds of stoneware, oxide of tin enters into the composition with the oxide of lead, and gives a whiter glaze. All the coarser kinds of pottery are glazed with oxide of lead, which promotes so much the fusion and vitrification, that the low heat at which they are baked is sufficient.

The colours on the surface of porcelain are obtained from metallic oxides, and applied by fluxes, or enamels more fusible than the matter of the porcelain. On this subject, some information has been given by Clouet * and Brongniart †. The flux generally employed to fix the colouring matter, is either a mixture of vitrified oxide of lead and silex, or borax, or sometimes a mixture of all these. By promoting the fusion of the metallic oxide, it causes it to adhere at a lower heat than that by which it might be decomposed, and the colour changed; it also serves as a medium of union with the matter of the porcelain, and ren-

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* Philosophical Magazine, vol. vii. p. 1.

† Nicholson's Journal, 8vo, vol. iii. p. 101.

ders the surface more smooth. The method of applying it is, either to mix the metallic oxide, or mixture of oxides, which is to give the colour, with the materials of the flux, the whole being reduced to an impalpable powder, which is made into a thick liquid, with gum-water, or with a volatile oil, and applied, by a pencil, to the surface of the unglazed porcelain; or, the colouring matter and the matter of the flux are fused together, and the enamel thus formed, being reduced to a fine powder, is applied in a similar manner. The first mode is generally employed with those colours which are liable to be altered by heat.

The oxides of different metals give different colours. Carmine red is obtained from the purple precipitate of the solution of gold by muriate of tin: violet from the same substance, when a larger quantity of oxide of lead is contained in the flux; rose-red from oxide of iron, highly oxidized by the action of nitric acid: yellow, from a mixture of white oxide of antimony with oxide of lead and silex: blue, from oxide of cobalt: green, from oxide of copper; and brown, from various proportions of oxides of manganese, copper, and iron mixed. In gilding porcelain, the gold obtained in a state of mechanical division, or perhaps slightly oxidated by decomposing the nitro-muriate of gold by heat, is applied by the medium of borax and gum-water, and, after having been fixed by baking the porcelain, is burnished. Platina is applied in a similar manner.

That variety of earthen ware of which retorts and crucibles are formed, is formed from a clay in which alumina and silex are contained, or at least with the addition only of oxide of iron, and which, therefore, is extremely refractory. The clay of which the Hessian crucibles are manufactured, consists, according to Vauquelin's analysis of it, of 69 of silex, 21.5 of alumina, charcoal 1, and 8 of oxide of iron. Brick and tile are made from the coarsest clays, exposed to a less strong heat.

Alumina fuses with some metallic oxides, forming glasses or enamels more or less perfect. It exerts no action on the metals or the simple inflammables.

It unites with the acids, and neutralizes the acid properties. Its salts are in general soluble; those of them which are so, are distinguished by a peculiar taste, sweetish, and astringent. All its saline combinations are decomposed by the alkalis; the acid being abstracted, and the earth partially precipitated. By an excess of either of the fixed alkalis, it is re-dissolved. They are not precipitated by prussiate of potash. The test by which they are best distinguished, is to add to a strong solution of any of them sulphuric acid, with a little potash, leaving the acid in excess; crystals of alum in octohedrons soon form.

Carbonate of Alumina.—It is doubtful if this compound can be formed. Water impregnated with carbonic acid dissolves, according to Th. Saussure, a portion of the earth, but in evaporating the solution, the carbonic acid is expelled. In decomposing an aluminous salt by an alkaline carbonate, the alumina which is precipitated has a portion of carbonic acid combined with it; but it appears also to retain a portion of the alkali employed in the precipitation.

Nitrate of Alumina.—The solution of alumina in nitric acid becomes gelatinous on evaporation, and soft crystalline scales are formed. This saline matter has generally an excess of acid: its taste is sour and astringent: it is very soluble in water, and deliquesces on exposure to the air. When exposed to heat, it is decomposed; its acid being expelled without decomposition, the heat requisite for its expulsion being less than that necessary to decompose it. According to Dalton it consists, exclusive of water, of 28.3 of base, and 71.7 of acid.

Sulphate of Alumina.—The salt known by the name of Alum was supposed to consist of the combination of sulphuric acid and alumina, with an excess of acid, but it always contains potash or ammonia; and hence differs from the proper sulphate of alumina.

When the pure earth is dissolved in sulphuric acid, it is difficult to bring so much into combination as to neutralize the acid; but, by boiling the solution with an additional portion of argillaceous earth, the neutral compound is obtained. It crystallizes in thin scales, white, and of a pearly lustre, which alter little by exposure to the air: its taste is astringent: it is very soluble in water: when exposed to heat, its water of crystallization is dissipated, and by a stronger heat, its acid is expelled. According to Bergman, it consists of 50 of alumina, and 50 of sulphuric acid: according to Dalton, of 30.6 of base, and 69.4 of acid. When combined with an excess of acid, the compound crystallizes with more difficulty, as, on evaporation, it assumes a gelatinous consistence. Small brilliant crystals, however, are formed in it.

Alum.—The salt to which this name is given is different from the Alumen of the ancients, which appears to have approached more nearly to a sulphate of iron. It was discovered prior to the 15th century; the method of obtaining it was imported at that period from the Levant into Italy, and was soon afterwards practised in different countries. It was procured from certain varieties of slate by an artificial process, consisting in general of calcination, exposure of the calcined matter to the air, lixiviation, and crystallization. Pott and Margraaf first shewed that its base is argillaceous earth.

In the manufacture of alum, from what were thus named Alum Ores, it was usually found necessary to add a portion of alkali, either potash, or an impure ammonia, to cause the salt to crystallize. The operation of this was supposed to be, the correcting the too great excess of acidity, which, it was imagined, prevented the crystallization. Bergman observed, that soda or lime does not promote the crystallization: he also found, that potash exists in several of the varieties of alum of commerce, but he appears to have regarded it as accidental, not essential to their composition. This subject was investigated about the same time by Vauquelin, and by Chaptal *, who proved, that the sulphate of alumina, either neutral or acidulous, cannot be crystallized but with difficulty, and in small plates; but that, on adding to the concentrated solution a little of a solution of potash, the crystallization commences, and, by adding the requisite quantity, the whole may be obtained in the state of crystallized alum. The same effect was obtained from the addition of sulphate of potash.

The alum of commerce is generally a super-sulphate of alumina and potash. According to Vauquelin's mode of stating the results of his analysis, it consists of 49 of super-sulphate of alumina, 7 of sulphate of potash, and 44 of water; or of acid 30.52, alumina 10.50, potash 10.40, and water 48.58. Thenard has stated the composition at sulphuric acid 26.04, alumina 12.53, potash 10.02, water 51.41 †. Thenard, however, estimated the quantity of sulphuric acid by means of barytes, and adopting the estimate of 26 of acid in sulphate of barytes, instead of 33.5, has under-rated it; correcting this, it brings the sulphuric acid in alum to 33 *per cent.* and reduces a little the proportions of potash and alumina. Vauquelin has also under-rated the proportion of acid; for alum, when precipitated by barytes, gives about the same weight of sulphate of barytes, which contains in 100 at least 33 of acid. Mr Dalton, from an analysis by Mr Tennant, with some comparative results, assigns as the proportions 33 of acid, 11.7 of alumina, 8.3 of potash, and 47 of water ‡. Berzelius has stated them at 34.23 of acid, 10.86 of alumina, 9.81

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* Annales de Chimie, tom. xxii. p. 258, 280.

† Nicholson's Journal, vol. xviii. p. 282.

‡ System of Chemical Philosophy, p. 550.

of potash, and 45 of water; or sulphate of alumina 36.85, sulphate of potash 18.15, water 45 *. Alum, from its power of reddening the vegetable colours, is evidently a super-sulphate. Mr Dalton maintains, however, that this effect is owing to the affinity of the alumina to colouring matter, so that the salt is decomposed, and as much acid is evolved, as causes the reddening. The acidity, however, is too considerable to be accounted for on this supposition; and the effervescence which alum produces with the alkaline carbonates, appears to establish the excess of acid in its composition. In the process of its formation too, super-sulphate of potash is preferred by the manufacturers, and sulphate of potash does not succeed so well.

In some of the varieties of alum, ammonia is a constituent ingredient, it having been found that the addition of an impure ammonia to the ley from the calcined alum ore promotes the crystallization; and as this can be economically procured from bones or urine, it is often added along with a portion of potash. The presence of this ammonia is discovered by its smell, when lime is added to a solution of the salt. There is one sub-species of what has been called alum, which is said to consist of sulphuric acid, alumina, and ammonia. This must be a different salt from that which contains potash, but the distinction in properties appears not to be considerable, and has scarcely been pointed out: it is not met with in the varieties of alum in this country. It is probably in the state of this salt that ammonia exists in that variety of alum in which this alkali is found with potash, and that the two triple salts, the sulphate of potash and alumina, and sulphate of ammonia and alumina, form the proper species. In almost all the varieties of alum, a minute quantity of iron is present, as an accidental ingredient, in the state of sulphate; this appears, from the experiments of Thenard, to have an in-

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* Annales de Chimie, tom. lxxxii.

jurious effect in dyeing on some of the more delicate colours, especially in silk dyeing, and to this freedom from iron is owing the preference that has been given to Roman alum *. The English alum is often contaminated with iron.

Alum is often a natural product. It occurs efflorescent, in the layers of a species of slate, which, from producing this salt, has received the name of Alum Slate. This contains sulphur, probably in the state of sulphuret of iron; from exposure to the air, the sulphur is oxygenated, and converted into sulphuric acid, which re-acts on the alumina, the basis of the slate, and combines with it; and the process is probably much facilitated by the presence of the iron: the sulphuret of iron first suffering oxygenation, and being converted into sulphate of iron: and this salt continuing to absorb oxygen, passes to the higher state of oxidation, in which the oxide retains the acid with less force: the latter, therefore, is more easily attracted by the alumina, and by the progress of these changes, the whole nearly of the acid is transferred from the oxide of iron to the argillaceous earth. As the alum effloresces in regular crystals, potash must also be present, and indeed, from Klaproth's analysis, is proved to be contained in the native slate. Vauquelin found, in one fossil of this kind which he analysed, that which affords alum at the celebrated works at Tolfa, near Civita Vecchia, potash, in the quantity of 3.4 *per cent.*

In a large coal-mine near Glasgow, which has been wrought at least 200 years, the aluminous slate above the coal has been fully exposed, and the circumstances being favourable for the production of native alum, the formation has taken place to a great extent, accompanied with a production of sulphate of iron †.

In circumstances which are not favourable for the natu-

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* Annales de Chimie, tom. lix.

† Nicholson's Journal, vol. xvi. p. 255.

ral oxygenation of the sulphur in the alum slate, and the consequent formation of alum, an artificial process is followed. The alum ore, as it is named, is calcined, by which the aggregation is subverted, and the sulphuret is brought into that state by which it most readily absorbs oxygen; this is completed, so as to convert it into sulphuric acid, by exposing the calcined ore to the air, with the presence of humidity; the process being probably aided in this, as in the natural formation, by the presence of iron: an acidulous sulphate of alumina is formed, which is extracted, by washing the materials with water. From some varieties of the alum-stone, as, for example, from that of La Tolfa, the alum crystallizes without farther addition; but in general, from the absence of the proportion of potash, requisite to the constitution of the salt, there is added a solution of the potash of commerce, or, what is now more economically used, the acidulous sulphate of potash, obtained in the distillation of nitric acid, or the muriate of potash, contained in the residual liquor from the manufacture of soap; or sometimes a ley from kelp, which contains both muriate and sulphate of potash; and, by evaporation, the alum is obtained by crystallization. The muriate of potash answers equally well with the sulphate, and there is one reason for even preferring it,—that while its potash unites with the sulphuric acid and alumina, to form the alum, its acid combines with the oxide of iron usually present; and muriate of iron being little disposed to crystallize, the contamination of the alum with iron, which is so prejudicial, is avoided.

Alum, as it is usually met with, is in large masses destitute of figure, but of a crystalline texture, transparent, and colourless. What is named Roch Alum in commerce is in small crystalline fragments, less transparent, and of a red tinge. The form of the regular crystals is an octaedron. It is soluble in 15 parts of cold, and in less than its weight of boiling water: its crystals are slightly efflorescent: its taste is sweetish and astringent. Its solution reddens the vegetable colours, from the excess of acid. Alum exposed to a very moderate heat suffers the aqueous fusion. As the water evaporates, it leaves a light white powder, named Burnt or Calcined Alum. By a strong heat, the acid is partly expelled, partly decomposed, a quantity of oxygen being afforded by its decomposition.

This salt is decomposed by the three alkalis, and by barytes, lime, and magnesia, which attract the greater part of the acid, and precipitate the earth.

A different decomposition which it suffers, is that from the action of carbonaceous matter at a high temperature; the oxygen of its acid is partially abstracted, and a sulphite of alumina remains. A decomposition of this kind, in which a large proportion of carbonaceous matter is used, affords a product which burns spontaneously on exposure to the air. This substance, named Pyrophorus, and discovered by Homberg and Lemery, is prepared by exposing to heat in an iron-pot, two parts of alum, with one part of flour: the mixture liquefies, and is to be stirred constantly till the whole becomes grey, and easily reducible to powder while hot. The coarse powder is put into a coated phial, so as nearly to fill it: the mouth of the phial is closed lightly with a small plug of clay, and is placed in a crucible, and surrounded with sand to the neck. The crucible is heated to redness, until a blue flame appears at the mouth of the phial: when this has continued ten minutes, it is removed from the fire, and the phial, when cold, is accurately stopt.

This substance inflames in atmospheric air: in a moist atmosphere the inflammation is more speedy, and in a dry air it scarcely takes place. It burns brilliantly in oxygen gas, in nitrous gas, and oxymuriatic acid gas, and is inflamed by sulphuric and nitric acids. It has been proved, that in order to form Pyrophorus, the alum must contain potash; the theory usually given of its preparation, and of its spontaneous inflammation, was, that the carbon of the vegetable matter decomposes the sulphuric acid, carbonic acid or oxide, with sulphurous acid and sulphuretted hydrogen gases, being disengaged; the potash of the alum combines with a portion of sulphur, forming a sulphuret, which is intimately diffused through the argillaceous earth: a quantity of charcoal remains in the same intimate mixture, and all these substances are perfectly dry. When exposed to the air, moisture is absorbed by the sulphuret, by which the temperature is raised, and the water is decomposed: the sulphur, by a disposing attraction, absorbs oxygen, is inflamed, and thus kindles the dry carbonaceous matter; the inflammation of both being facilitated by their division, from their intimate mixture with the argillaceous earth, and the extensive surface they present to the air. It is not improbable, however, as Davy has suggested, that the inflammability may be connected with the presence of potassium, produced by the joint action of the charcoal and sulphur on potash. Dr Coxe has found, that when pyrophorus has lost its property of spontaneous inflammability, it may be restored by moistening it with a solution of potash, and again exposing it to heat, until there is the appearance of a rose coloured flame, a fact conformable to this view *.

Alum is used in a variety of arts. It hardens tallow: it increases the adhesive power of the farinaceous pastes: it renders water clear, which is turbid from the admixture of earthy particles; it is used in tanning; and it is of essential use as a mordant in the art of dyeing, fixing the colours, and often adding to their brilliancy. It is used in medicine as a powerful astringent.

If a solution of alum be boiled with argillaceous earth, it becomes insoluble, and is precipitated in a powder, which is insipid: this is either a sulphate or sub-sulphate of alu-

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* Annals of Philosophy, vol. i. p. 68.

mina and potash. Mr Dalton, however, was unable to form it. From the experiments of Chaptal, it appears, that an excess of potash may enter into the composition of alum so as to alter its properties: with a certain quantity, the salt crystallizes in cubes, and, with more, it falls down in flocculi *.

SULPHITE OF ALUMINA.—Sulphurous acid gas passed through water, in which alumina is suspended, combines with it, and forms a compound, which is insoluble, and which, when dry, is in the state of a white powder, soft to the touch, and having a sulphureous taste. Its acid is expelled by heat. From exposure to the air, it passes to the state of sulphate.

PHOSPHATE OF ALUMINA.—When phosphoric acid is combined with the earth of alum to saturation, it forms, according to Fourcroy, a white insipid powder; insoluble, which melts before the flame of the blowpipe into a transparent globule.

PHOSPHITE OF ALUMINA is prepared by adding aluminous earth to phosphorus acid. The solution on evaporation becomes glutinous, but does not crystallize. It is soluble, and has a styptic taste. By heat it is not easily fused, but is rather decomposed.

BORATE OF ALUMINA.—When aluminous earth, newly precipitated, is digested with boracic acid, there is deposited, by continuing the evaporation, a viscid substance, through which minute crystals are interspersed, having a very astringent taste, and which is probably borate, or rather super-borate of alumina.

MURIATE OF ALUMINA.—Muriatic acid dissolves aluminous earth with facility. The solution can scarcely be brought to crystallize, but forms, by evaporation, a gelatinous mass, which is deliquescent, and is decomposed by heat, its acid being expelled. It has the astringency of

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* Annales de Chimie, tom. xxii.

the other aluminous salts, and usually, perhaps always, has an excess of acid. Mr Dalton has stated its composition at 59.5 of acid, and 40.5 of base.

OXYMURIATE OF ALUMINA.—This combination has been established by Mr Wilson by a process of double decomposition,—mixing a solution of oxymuriate of lime, prepared in the usual manner, with a solution of alum. The solution of oxymuriate of lime is prepared of the specific gravity 1.060, and the solution of alum of the specific gravity 1.100; the latter is added to the former as long as any precipitation takes place; the sulphuric acid of the alum combines with the lime, and a copious precipitate of sulphate of lime is deposited; the clear liquor above contains the oxymuriatic acid combined with the alumina, forming a soluble compound. A slight smell of oxymuriatic acid is perceived on the first addition, probably from the action of the excess of sulphuric acid in the alum; but this is soon removed. The liquor retains completely the power of destroying colours; the rapidity of its action is even greater, it is remarked by Mr Wilson, than a solution of oxymuriatic acid, as the alumina fixes more of the gas than water would condense alone; and still, from the weak affinity with which it retains it, does not seem to take away any of its discharging power. He has applied successfully this combination to a particular purpose, that of discharging the Turkey red dye, an operation often performed in calico-printing on parts of the cloth, to diversify the design. The colour of this dye is so permanent, that it resists the action of oxymuriatic acid in combination with any of the bases before employed, potash, lime, or even magnesia; it was necessary therefore to employ a solution of the oxymuriatic gas in water. But the noxious vapour arising from this rendered some other method highly desirable. Mr Wilson found, that the solution of oxymuriate of alumina answers the purpose completely, and he states that it has been extensively applied. It may also be employed in the bleaching of fine cloth, especially where, in the subsequent dyeing, it is of importance that oxymuriate of lime should not be used, or where alumina itself is to be used as a mordant *.

FLUATE OF ALUMINA.—This salt, Gay Lussac states, is obtained on pouring neutral fluate of potash into a solution of alum; it is immediately precipitated in a pulverulent state. It is insipid, insoluble in water, and soluble in an excess of acid; after being dried rather strongly, the acids do not act on it but with difficulty †.

CHAP. VI.

OF SILICA OR SILEX.

THIS Earth is possessed of very peculiar characters. In its physical qualities, its infusibility, insolubility in water. its comparative inertness as a chemical agent, and its relations to the greater number of bodies, it resembles the other earths; and it is associated with them by existing as a constituent ingredient of the mineral compounds which they form. But it is remarkably distinguished by one character, that of not uniting with acids, and thus of not forming neutral salts. In this respect, and comparing it with its other properties, it may be regarded as a body nearly insulated. Still, on the whole, it approaches to the earths, and is connected with them by its most striking relations; and even in the exception which it presents with regard to the acids, the analogy is preserved in its uniting in the humid

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* Annals of Philosophy, vol. viii. p. 125.

† Recherches Physico-Chimiques, tom. ii. p. 27.

way with fluoric acid, and in the dry way with the phosphoric and boracic acids.

A singular opinion has been advanced, that silica may be ranked as an acid. This appears to have been suggested by Mr Smithson*, and has been adopted by Berzelius. It is founded on the circumstance, that in the mineral kingdom it exists combined with the different earths, and in these compounds it is supposed that the silica acts as an acid, combined with the particular earth as a base; and Berzelius has accordingly described a number of these compounds as Siliciates †. This, however, is altogether vague. The property of combining with an alkali or earth, is insufficient to establish such a conclusion, for each earth combines with others, and more or less with the alkalis. Alumina, for example, combines as intimately with potash as silica does, and with more facility; it equally unites with barytes, strontites, lime, and magnesia, and with attractions apparently as strong; yet it cannot be ranked as an acid, since it neutralizes the acids. In one point of view, perhaps, all the compounds of earths with each other, or even with the alkalis, or with metallic oxides, may be considered as analogous to salts, for both orders are probably ternary compounds of two oxidifiable bases with oxygen; and in some of the salts, the arseniates, or chromates, for example, the two bases are even metallic. But in this respect there is nothing peculiar to silica; it presents no point of resemblance greater than the others, nor have the compounds of this earth with the alkalis and the other earths the least resemblance in their properties to salts. There is therefore nothing in the chemical agency or combinations of silica to justify this opinion; no body is more remote in its properties from acidity, and it is to confound

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* Philosophical Transactions, 1811, p. 176.

† Essay on Chemical Mineralogy.

all chemical distinctions, to associate it with substances so totally different.

Siliceous Earth* is the principal constituent part of a great number of earths and stones,—Rock Crystal, Quartz, Flint, Sandstone, and others. In some specimens of rock crystal it forms 99 parts in 100; in flint it is nearly equally pure, amounting to 97 or 98 parts. It is generally procured from flint. The usual process is to calcine common flint in a crucible, in an open fire, so as to render it brittle. One part of this reduced to powder is mixed with three or four parts of sub-carbonate of potash, and exposed, in a silver bason, to a heat gradually raised, until the mixture is fused; it is to be kept in fusion for a short time; when cold, it is dissolved in water, the siliceous earth of the flint being rendered soluble by its combination with the alkali. To the solution diluted sulphuric acid is added as long as any precipitation takes place: the precipitate is washed with water, until the water come off tasteless, and is then dried. If the fusion has been performed in a crucible, the silica is mixed with alumina, from the earth of the crucible; but avoiding this intermixture, it has been supposed to be obtained by this process pure. Mr Dalton has inferred, however, that it retains a portion of alkali in combination with it, and is thus analogous to glass. This is proved by the quantity of acid required for its precipitation not being more than half of that which the alkali in the compound would require for its saturation, and by the precipitate melting into glass before the blowpipe. Pounded rock crystal will therefore give the earth in a purer form; or a process recommended by Mr Dalton is, to decompose its solution in fluoric acid by ammonia; the precipitate he

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* Dr Pearson changed the term silex into silica, on the principle of giving the names of the earths a similar termination; and this term being now generally received, I have in general adopted it.

regards as the pure earth, though it is not improbable that it may be a sub-fluate *.

Sir H. Davy, in attempting to decompose siliceous earth by galvanism, found, that it is little affected, partly from its insolubility, and partly from its being nearly in a state of indifference with regard to the negative or positive pole, resting equally at either, when placed in the electrical circuit, diffused in water. By employing the methods described under the history of alumina, appearances of decomposition were however obtained. Thus, when the silica was fused with six parts of potash, in the galvanic circuit, metallic matter was obtained, from which, when exposed to the air, or dropt into water, a minute quantity of earth was regenerated. A similar result was obtained, by electrifying negatively potassium, amalgamated with one-third of mercury, in contact with siliceous earth; and on submitting it to the action of potassium in contact with iron, or with mercury, products were obtained, from which, by solution in acids, the earth was re-produced †. In a subsequent series of experiments ‡, potassium was passed in excess over silica in a heated tube of platina; the result consisted chiefly of alkali, containing a dark coloured powder diffused through it; the whole was fused with sulphur, which combined with the alkali; on dissolving this in water, the dark coloured matter separated, but the water at the same time acted upon it, producing gas, and the whole nearly was converted into silica. This matter, Silicon, or Silicium, as it has been named, Sir H. Davy has supposed to be the base of this earth; and if this opinion be just, as it has no metallic appearance or properties, silica would differ in chemical constitution from the other earths: he

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* Chemical Philosophy, p. 558.

† Philosophical Transactions, 1808, 1810.

‡ Ibid. 1814, p. 67.

regards it as an inflammable body, analogous to boron. The experimental results, however, are evidently too imperfect to establish any certain conclusion. On the assumption that silica has a metallic base, this substance, if it is a product free from any combination with potassium, may be an oxide at a low degree of oxidation. It seemed to be soluble in a strong solution of potash, communicating to it a tint of olive.

Berzelius had endeavoured to decompose silica by exposing it in mixture with charcoal and iron-filings, to a heat sufficient to melt the iron, supposing, that if it contained a metallic base, its decomposition by the charcoal might be aided by the affinity between this base and the iron. Globules were obtained, some of a silvery white colour and malleable, others brittle and black, surcharged with carbon. When burnt, both afforded siliceous earth; and it was also obtained from the alloy by the action of acids. He inferred, therefore, that " silica is by means of carbon reduced to a body, which enters into union with iron, and which, not injuring the malleability of the iron, must be of a metallic nature *." This experiment has been repeated with success by Stromeyer.

Berzelius endeavoured to determine the quantity of oxygen in silica, by finding the quantity of iron and carbon in the alloy, from the results of the action of an acid upon it; ascertaining in this way how much silicium it contained, and, lastly, finding what quantity of silica this afforded, and of course with what quantity of oxygen it had combined. The results gave as the composition of silica, 38 of base, and 62 of oxygen; which, however, he found reason to correct to 51.5 of base, and 49.5 of oxygen; and subsequently to state at from 45.3 to 47.7 *per cent.* of oxygen, differences so great as to render the determination very doubtful. Stromeyer, from his analytic experiments,

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* Philosophical Magazine, vol. xl. p. 201.

inferred, that the proportion of oxygen is as high as 55 *per cent.*[*]. Sir H. Davy ascertained, that it requires more than three parts of potassium to decompose one part of silica, whence, if this result be correct, it follows, that it cannot contain much less than half its weight of oxygen.

Silica occurs in nature crystallized, forming quartz or rock crystal; obtained by precipitation, it is in the form of a white powder, the specific gravity of which is about 2.6. It is insipid, and is harsh and gritty to the touch: it does not form with water an adhesive paste.

This earth is extremely infusible. It not only does not melt in the focus of the most powerful burning mirror, but, according to the experiments of Lavoisier[†], confirmed by those of Guyton[‡], it remains without fusion when in the state of rock crystal, in the more intense heat excited by oxygen gas directed on burning charcoal. Mr Hare found it to melt in the flame of a stream of oxygen and hydrogen gases; it formed a kind of enamel[||]. Some observations appear even to prove that it may be volatilized by intense heat, and that its vapour condenses in crystalline filaments[§].

It is very sparingly soluble in water, and under common circumstances appears insoluble. Bergman, however, observed, that when the silicated potash, or liquor prepared from dissolving in water the compound of silica and potash, is decomposed by an acid, if the solution has previously been largely diluted with water, no precipitate appears, nor is it even rendered sensibly turbid,—a proof that when in a state of division, silica is to a certain extent soluble in water. It has since been discovered to exist

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[*] Annals of Philosophy, vol. iii. p. 251.

[†] Mémoires de l'Acad. des Sciences, 1783, p. 566.

[‡] Journal de l'Ecole Polytech. Cah. III. p. 298.

[||] Philosophical Magazine, vol. xiv. p. 304.

[§] Geological Transactions, vol. ii.

frequently in mineral waters in solution. In the water of the Geyser fountain in Iceland, it is present to the amount of 9 or 10 grains in 100 cubic inches of water: and although a small quantity of alkali is also present, amounting, according to Dr Black, to 1.5 grains, according to Klaproth, to 3 grains; this, from what we know of the power of the alkalis to hold it in solution, is, independent of the solvent power of the water, in too small quantity to dissolve this proportion: the alkali, too, is in the state of carbonate, by which its solvent power is diminished. It also exists in solution in other mineral springs, in which no alkali, nor any substance that can contribute to its solution, can be detected *. And quartz stalactites occur, with their surface covered with minute crystals,—a proof of the deposition of silex from a state of solution. In the gelatinous form in which silica is precipitated from its solutions, it is probably a hydrate; but it retains the water constituting this with little force. It exists in nature, however, in more intimate combination with water, the opal, and some analogous fossils, containing about 10 in 100 of combined water.

The chemical relations between silica and the fixed alkalis are important. They form very perfect combinations, which differ in their properties, according to the proportions. With a large quantity of alkali, the compound is soluble in water; with a smaller quantity it is insoluble.

The combination can be effected even in the humid way. If on silica, in a state of extreme division, an alkaline solution be boiled, a quantity of the earth is dissolved, and the liquor forms a jelly on cooling.

If any pure siliceous fossil, as quartz, or flint, reduced to powder, be exposed, with three parts of sub-carbonate of potash, to a heat raised to redness, they enter into fusion; the materials swell, and an effervescence takes place

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* Nicholson's Journal, 4to, vol. iii. p. 403.

from the disengagement of water and carbonic acid: a species of glass or frit is formed, which is deliquescent on exposure to the air. When water is added, a solution is effected; part of the earthy matter being in general left undissolved: the matter dissolved is the compound of the earth with the alkali, retaining a little carbonic acid. If pure potash has been employed in the experiment, the fusion is more complete, the glass formed more perfect, and entirely soluble in water. When the solution of silicated potash or soda, *Liquor Silicum*, as these compounds have been named, is concentrated by evaporation, it assumes a gelatinous consistence. By large dilution with water, it is partially decomposed, and a portion of silica is precipitated. It is decomposed by all the acids, even by the weakest, and the earth is thrown down in the form of a spongy precipitate.

Silica, either pure, or in combination with a little alkali, appears to be capable of crystallizing from this liquid. Trommsdorff having observed, that, in a bottle in which liquid silicated potash had stood for eight years, crystals were deposited, tetraedral pyramids, transparent, and so hard, that they gave sparks with steel: they were soluble in liquid potash, and in fluoric acid *.

When a smaller proportion of alkali is employed, the compound is less soluble in water, and a stronger heat is required for its vitrification; and when the proportion of alkali is not more than half that of the earth, it is transparent, permanent in the air, and insoluble in water. This is the well-known compound Glass, one of the most beautiful and useful products of art. The following is an outline of the process by which it is formed:

Two parts, by weight, of siliceous earth, are mixed with from one part to one and a half of carbonate of potash, or soda, of commerce. These are the essential ingredients

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* Annales de Chimie, tom. xxii. p. 118.

of glass: they are intimately mixed, and the mixture is exposed to a strong heat in a furnace, to expel the water and carbonic acid, and to effect an imperfect combination between the alkali and earth. This forms what is named the frit. Large pots made of clay, and placed in a furnace, are filled with it, heat is applied sufficient to fuse it, and the melted mass is kept in fusion till the whole appears to be uniform. This forms the glass, which is then ready to be worked. The unvitrified matter is withdrawn.

The transparency and other estimable qualities of the glass, are greater, as the materials have been pure. The finer kind, crystal glass as it is named, is from the best pearl ash with pounded flint, or a very white sand washed. Window glass is from sand and kelp. Green bottle glass is from sea-sand, and the refuse of the soap-maker's ley, which contains more lime than alkali. The proportions of the ingredients have likewise an influence on the qualities of the glass. The less alkali is present, the more heat is requisite for the vitrification; but the glass is also harder, and less liable to be altered by exposure to air or moisture. Though the alkali and siliceous earth produce a perfect glass, yet other additions are made for different purposes. The most essential is that of oxide of lead. It promotes the vitrification of the materials; and it renders the glass more dense and ductile, and susceptible of a higher polish, and adds much to its refractive power, and of course to its lustre. Hence it enters largely into the composition of ornamental glass, and of flint glass or crystal. It renders the glass at the same time softer, and therefore more liable to be scratched; it gives also more fusibility.

Another metallic oxide used in the preparation of the finer kinds of glass, is black oxide of manganese. It is added to improve the whiteness and transparency. Its operation is principally on the oxide of iron, which is contained in the materials, and the theory of its action was very well explained from the researches of Scheele, by

Bergman. Iron, in a low state of oxidation, gives to glass a green tinge, while, at a high degree of oxidation, it either does not enter into fusion with the ingredients of the glass, or it does not communicate colour. Manganese, on the contrary, in the state of black oxide, gives a violet colour, while, in a lower state of oxidation, the glass is colourless. In adding, therefore, the black oxide to glass, while it yields its oxygen to the iron which it thus brings to a high state of oxidation, it itself passes to the lower state, and each is in that state in which it does not communicate colour. To attain this, however, a certain proportion must be observed; for if there be an excess of the black oxide of manganese, it will produce a purple tint, while, if there be a deficiency of it, the green from the iron will prevail; and, accordingly, from the difficulty of fixing the precise proportion, glass has generally a slight shade of one or other of these colours. Nitre is sometimes used for the same purposes as the oxide of manganese. Borax enters into the composition of the glass used to imitate the gems. Oxide of arsenic is used as a flux, and to correct the purple tint from manganese.

When glass is in fusion, it has a great degree of tenacity and ductility; it has also the property of adhering to a metallic tube or rod. Hence it can be easily removed from the furnace, can be blown into any shape, be cast into molds, and cut and wrought in a variety of forms.

Though glass at a high temperature has so much ductility, at a low temperature it is extremely brittle. If it is hastily cooled, this brittleness is so great, that the slightest agitation, even that from the undulations of the atmosphere, is sufficient to break it into fragments. This is remedied by the process of annealing. The glass, after it has been blown or cast into vessels, is removed into a furnace, the heat of which is not sufficiently high to soften it; and the vessels are gradually removed from the hotter to the colder parts of this furnace. The brittleness of the glass hastily cooled, seems to be owing to the regular arrangement of the particles being disturbed ; and the utility of the gradual reduction of temperature consists in allowing this arrangement to take place.

Glass, properly prepared, is scarcely acted on by any chemical agent. With the exception of fluoric acid, the most powerful and concentrated acids may be kept in it without suffering any change. From the experiments on the repeated distillation of water from glass retorts, already stated under the history of that fluid, it appears, however, to be slowly eroded and decomposed at a high temperature, probably from the affinity exerted by the water to the alkali. When fused with an alkali, it is rendered soluble in water. And potassium and sodium decompose it from their strong attraction to oxygen, in consequence of which they partially abstract the oxygen from its alkaline, and perhaps also from its earthy matter. The alkaline sulphurets in solution form a dark coloured film on it, from their action on the oxide of lead it contains.

A singular change, to which glass may be subjected, is what is named its Devitrification. In the manufacture of glass, it sometimes happens that masses of it lose the glassy character, become opaque, and exhibit an appearance of crystallization in their structure, rays diverging from different centres; and it had been observed that glass assumed these properties when it had been slowly cooled from a state of fusion. This was investigated by Sir James Hall, who proved that the slow cooling is the cause of this change; a piece of green glass being made to assume the stony character, by slow cooling, after fusion, and being restored to the state of glass, when again fused and cooled hastily, and this repeatedly on the same specimen. He extended his experiments to various natural substances, varieties of basalt and greenstone, which, by fusion, afford glasses, and established the same fact with regard to them; and one still more singular, that the substance, when it has the stony character, is less fusible than when it has the vitreous, softening in the one state at from 15 to 24 of Wedgwood, in the other at from 32 to 38 *. The want of transparency and the crystalline structure may arise from the arrangement into which the particles of the fused substance are allowed to pass by slow cooling; but there is some difficulty in assigning an adequate cause for the fusibility of the substance being different in the one state from what it is in the other, at least if no separation of the principles of the glass, but merely a change in the state of aggregation, take place.

The change which glass suffers when it is exposed to heat, imbedded in gypsum, or in other earthy substances, by which it loses its transparency, acquires more hardness, becomes less fusible, and more capable of bearing sudden alterations of temperature, is probably of a similar kind. Glass thus changed has received the name of Reaumur's Porcelain; this chemist having first observed its production and properties.

A branch of the art of glass-making is that of imitating the Gems, or the making those coloured glasses named Pastes. The basis of these is a pure glass prepared from quartz, fused with an alkali, with the addition of borax, and oxide of lead. Different colours are obtained from the addition of metallic oxides: gold gives a red, cobalt blue, manganese purple, lead yellow, iron green; and these colours are so rich, as to be equal, or often superior, to those of the gems: though in lustre, hardness, and consequently in durability, the pastes are far inferior. They are easily distinguished by their inferior specific gravity, and their softness, which is such that they can be scratched by the knife. Very complicated recipes were formerly given for their preparation, which are collected in the works of Kunckel and Neri, and which have been gradually sim-

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* Edinburgh Philosophical Transactions, vol. v.

plified. A series of experiments, in which processes for imitations of the different gems are given, is inserted in the Journal de Physique, tom. xxviii. p. 502.

When glass is fused with a large quantity of oxides of tin and lead, it becomes white and opaque. This forms what is named Enamel. The Rice Stone, as it is called, of the Chinese, of which they form ornamental vessels, and with regard to which various opinions had been formed, is a fused enamel composed chiefly of silica with oxide of lead. Klaproth by analysis obtained from 100 parts of it, 39 of silica, 7 of alumina, and 41 of oxide of lead; the remaining 13 parts being probably some flux, borax, potash, or soda. Considering it as probable, that it is formed, not from the pure earths, but from feld-spar which enters into the composition, he found, on making the experiment which this suggested, that a similar substance is formed by melting 8 parts of oxide of lead, 7 of feld-spar, 4 of white glass, and 1 of borax; and also from 8 parts of oxide of lead, 6 of feld-spar, 3 of silex, and 3 of potash, soda, or borax. When in fusion, it can be pressed into a mold, and figures may be impressed on it; when solid, it is so hard as to scratch glass; in colour and semi-transparency, it is similar to alabaster, and its fracture displays a kind of waxy closeness and tenacity *.

Silica exerts affinities to the other earths. It unites with barytes by fusion, and their mutual attraction is also exerted in the humid way. If it be mixed with three parts of barytes, and be exposed to heat in a platina crucible, a compound is formed, which has not the acrid taste of barytes, nor does it slake with water, but is soluble in all the acids, the barytes communicating this solubility to the siliceous earth. It is precipitated too from its alkaline solution by barytes, the two earths entering into combination. Strontites exerts a similar action on it. Vauquelin

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* Annales de Chimie, tom. lxix. p. 302.

found, that when the former earth is mixed with one-third of its weight of the other, and exposed to a strong heat, a mass is formed, not capable of slaking in water; but when pulverized and boiled in water, a portion of it is dissolved, and from this solution silica is precipitated by nitric acid. The strong attraction between lime and siliceous earth is displayed, in lime-water producing a precipitate, when added to silicated potash; this precipitate being a compound of the two earths. These two earths unite also by fusion. When in equal parts, they melt, according to Kirwan's experiment, at a heat not exceeding 150° of Wedgwood, and form a white enamel, semi-transparent, and so hard as to strike fire with steel. When the proportion of lime is only one-fourth that of the silex, the compound is not fused at 156°. It has been supposed, that on the affinity which these two earths mutually exert, even in the humid way, depends in part the induration of mortar. This is, no doubt, principally to be ascribed to the intimate union of the lime with the water of the mortar, and perhaps to the gradual absorption of carbonic acid from the atmosphere; but the advantage derived from the intermixture of sand, though it is in part of a mechanical nature, is probably also partly owing to the affinity exerted between the siliceous particles and those of lime, and those limestones which contain silica, afford the best mortar. Between magnesia and silica the mutual attraction is weak. When mixed in equal weights, they do not unite but at a very intense heat,—that excited by oxygen gas directed on burning charcoal; they then fuse into a white enamel so hard as to scratch glass *.

Silica vitrifies with some neutral salts, particularly with borax, and the alkaline phosphates. It also combines by fusion with a number of the metallic oxides. It does not exert any action on the metals, or on the inflammables.

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* Mémoires de l'Acad. des Sciences, 1783, p. 600.

Silica is scarcely soluble in acids, and is not capable of producing a neutral compound, a property which, as has been already stated, distinguishes it from all the other earths, and forms, in contrast with its other properties, its leading character. By fusion it combines with boracic and phosphoric acid, and forms a transparent glass; and, in the humid way, when in that state of division in which it is when precipitated from its alkaline solution, it has been supposed to be dissolved in small quantity by these acids. Muriatic acid dissolves it more sensibly: the solution is limpid; when concentrated by evaporation, it assumes, according to Fourcroy, a gelatinous consistence, and, if boiled, is decomposed; the silica, with perhaps a portion of the acid, being precipitated in a granulated powder *. Fluoric acid, however, is the proper solvent of this earth; and they appear to combine in different proportions.

When fluoric acid is disengaged from fluor-spar, or any of its compounds, and siliceous earth is presented to it, a portion of the silica is immediately dissolved, and siliceo-fluoric acid gas is, however, formed. Its history has been already delivered.

When this gas comes into contact with water, it suffers decomposition; it is instantly rendered opaque, and is absorbed, and at the same time a copious precipitate is formed. The acid absorbed by the water retains a considerable portion of silica in combination with it; the precipitated earthy matter had also been supposed to retain a portion of the acid, but, according to Mr J. Davy, when sufficiently washed it is pure silica.

This liquid acid has been named Sub-silicated Fluoric Acid, as it contains less silica than the gas; but it ought rather to be named Super-fluate of silex, as it contains a larger proportion of acid. To determine its composition, Mr J. Davy first found the quantity of silica in the siliceo-

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* System of Chemistry, vol. iii. p. 297.

fluoric acid gas, by decomposing it by ammonia, which precipitates it entirely; the proportions he assigned were 61.4 of silex, and 38.6 of fluoric acid: he then found the quantity of earth which it deposites when it is absorbed by water, which of course would give the quantity it retained; from this it followed, that the compound combined with the water, is composed, exclusive of water essential to the acid, of 54.56 of silex, and 45.44 of acid *.

This super-fluate of silica is strongly acid; it is volatilized by heat; and evaporates slowly on exposure to the air, leaving scarcely any siliceous residue; it is decomposed by the alkalis and earths, which attract its acid: sulphuric and muriatic acids disengage from it siliceo-fluoric acid gas. The siliceo-fluoric acid gas, as it has been named, may perhaps be the neutral compound. It has always indeed been considered as highly acid, and it gives evident indications of acidity in affecting the vegetable colours, and in other properties. But these indications are ambiguous, as they are afforded only by the medium of water, or of humidity, by which the combination is subverted, and acidity produced. The opinion has been already noticed, which considers it as a compound of the hypothetical principle fluorine with silicon.

The liquid fluoric acid, it is affirmed, acts on siliceous earth; in this manner a neutral combination may perhaps be established, though the fact has not been well ascertained. Bergman relates an experiment in which crystals were obtained by such a solution †. Some finely pounded quartz had been put into a bottle with liquid fluoric acid, which was put aside slightly corked. At the end of two years, there were found at the bottom of the vessel, besides a mass of prismatic spiculæ, thirteen small crystals, resembling cubes with the angles truncated. These are said

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* Philosophical Transactions, 1812.

† Chemical Essays, vol. ii. p. 54.

to have had the essential properties of quartz; they do not appear to have been analysed by Bergman, however, so as to determine whether they consisted of pure silica, or of this earth combined with fluoric acid; according to Fourcroy, crystals formed in this manner are fluate of silex, fluoric acid being expelled from them by heat, or by the action of a concentrated acid; but this is doubtful.

The triple fluates of silica with the different alkaline and earthy bases, have been noticed under their individual history.

CHAP. VII.

OF ZIRCON.

This earth was discovered by Klaproth in the Zircon or Jargon, a gem brought from Ceylon. It was afterwards found in the hyacinth. It is extracted from the zircon, by reducing it to fine powder by repeated calcination, and fusing it with five or six times its weight of potash, keeping the mixture in fusion for two hours: the mass is then lixiviated with water, to extract the superfluous alkali. It is dissolved in dilute muriatic acid: this solution is boiled, to cause the deposition of the silica: the liquor is filtered, and carbonate of soda added, taking care to avoid an excess; carbonate of zircon is precipitated: from this the carbonic acid is expelled by heat, and the pure earth is obtained.

Mr Davy, by submitting zircon to the action of galvanism, in contact with potassium and mercury, or by heating it with potassium, obtained results indicating decomposition; the product decomposing water, and affording a white powder which had the characters of zircon. In the latter experiment too, the potassium was converted into potash, and minute particles were diffused through the mass, having metallic lustre.

Zircon, obtained by the process above described, is a white powder, insipid, and somewhat rough. When exposed, imbedded in charcoal, to the heat of a forge, it undergoes semi-vitrification: it becomes so hard as to give fire with steel; has a brilliant vitreous fracture; and is of a grey colour. In this state its specific gravity is 4.3.

When zircon in powder is mixed with water, it imbibes it, and forms a semi-transparent jelly, and it retains so much of this in drying, as to form a substance in appearance like gum. It exerts, therefore, some affinity to water, but it is not entirely dissolved by it. This gelatinous hydrate seems to contain about 0.20 of water.

Zircon is insoluble in the liquid alkalis, but is dissolved by the alkaline carbonates. Its relations to the earths are scarcely known. It may be fused with silica and alumina, and a mixture of these three earths is more fusible than a mixture of two of them. It appears to combine too by fusion with some of the metallic oxides. On the inflammables it exerts no action.

It combines with the acids, and forms salts in general sparingly soluble. Those which are soluble have a sweetish astringent taste. These compounds are not easily formed by direct combination, unless the earth is in a loose state, as when it is newly precipitated; when it has been hardened by heat, it is scarcely acted on. Its affinities to the acids appear to be weak, as its salts are in general decomposed by a low heat, as well as by the alkalis, and all the other earths. Their solutions, if not too dilute, are rendered turbid by sulphuric acid, and a precipitate of sulphate of zircon is formed. When they are decomposed by the alkaline carbonates, if an excess of the carbonate be added, the precipitate is re-dissolved; and this effect produced in particular by carbonate of ammonia, serves to distinguish this earth from alumina. They give a white precipitate with infusion of galls, but are not precipitated by the alkaline hydro-sulphurets. The salts of zircon have been principally examined by Vauquelin *.

Carbonate of Zircon is insoluble, and when obtained by precipitation, appears as a white powder. It is decomposed by heat. When re-dissolved by an excess of the alkaline carbonate, a ternary combination of the zircon with the alkali and the carbonic acid is probably formed.

Nitrate of Zircon is not easily obtained perfectly neutralized: the solution of the earth in the acid when evaporated affords a transparent resinous-like matter, not easily dried, having an astringent taste. It does not form with water a proper solution, but rather gelatinous flocculi.

Sulphate of Zircon.—When sulphuric acid is digested on zircon newly precipitated, their combination is effected, and by evaporation to dryness, a sulphate is formed, insipid, and insoluble, partially decomposed by water, and easily decomposed by heat. With an excess of acid, a solution is formed, which affords a congeries of crystals, soluble in water, and having a styptic taste.

Phosphate of Zircon is insoluble.

Borate of Zircon is also insoluble.

Muriate of Zircon has an astringent taste, is very soluble in water, and in alkohol; by evaporation of its watery solution it forms transparent needle-like crystals, which are efflorescent.

Fluate of Zircon.—This salt is formed, according to Gay Lussac, on adding a solution of the earth in muriatic acid, with an excess of acid, to fluate of potash slightly acidulous; it is precipitated neutral, and altogether insoluble in water.

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* Annales de Chimie, tom. xxii.

CHAP. VIII.

OF GLUCINE.

HAUY observing an identity of crystalline forms in the beryl and the emerald, Vauquelin, on submitting them to analysis to elucidate this, discovered this earth as a constituent part of both *; and at a subsequent period, he undertook a more minute examination of its properties †. His experiments were confirmed by Klaproth ‡, and some observations on its properties were added by Ekeberg ||. It has some analogy to alumina in some of its properties, but it differs altogether in others. Its name of Glucine is derived from the property it has of forming salts having a sweet taste.

The process by which Vauquelin first obtained Glucine, was to fuse one part of beryl in powder with three of potash, in a silver crucible; the mass, after cooling, was diffused in water, and dissolved in muriatic acid: the solution is then evaporated to dryness, and, on again dissolving it in water, the silex present remains undissolved. The solution is decomposed by sub-carbonate of potash: the precipitate is digested with a solution of pure potash; the greater part of it, consisting of alumina, with a portion of glucine, is dissolved; but there remains a portion undissolved, which is the glucine, coloured by a small portion

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* Nicholson's Journal, 4to, vol. ii. p. 358, 393.

† Annales D'Histoire Naturelle, tom. xv. p. 9.

‡ Analytical Essays, vol. ii. p. 176.

|| Journal des Mines, tom. xii. p. 25.

of oxide of iron. A subsequent process which he employed to free it more perfectly from alumina, was to fuse the beryl with thrice its weight of potash,—diffuse the mass in water, and dissolve it by muriatic acid; evaporate the solution to dryness, re-dissolve in water, and separate by filtration the siliceous earth: then precipitate the solution by ammonia; re-dissolve the precipitate by sulphuric acid diluted, add to the solution sulphate of potash, and cause it to crystallize: by repeated crystallizations, the alumina is removed; the residual liquor, which is thick and viscous, is diffused in a large quantity of water, and carbonate of ammonia is added, until it is so far in excess as to leave the ammoniacal smell; it is put aside for 24 hours, and is then filtered to separate some traces of iron and alumina; and it is lastly made to boil to volatilize the carbonate of ammonia; the carbonate of glucine is precipitated in small spherical concretions, extremely light and white; by exposure to heat, it loses about half its weight, and the pure earth remains, retaining the same whiteness and volume *.

Sir H. Davy, in attempting the decomposition of Glucine, obtained results similar to those from zircon, an amalgam being formed, when it had been placed in the galvanic circuit with mercury and potassium which decomposed water, and which reproduced glucine, when the alkali in the liquid was neutralized by an acid. And a similar result was obtained by the action of potassium at a high temperature. Berzelius from indirect results has inferred, that it is composed of 69 of base, and 31 of oxygen.

Glucine is perfectly white; soft to the touch, and adheres to the tongue: it is insipid: is infusible: insoluble in water, but forms with it a paste which is somewhat ductile; this paste is not hardened by heat, nor does it contract. It melts with borax into a glass. The specific gravity of the earth is 2.96.

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* Annales du Museum d'Histoire Naturelle, tom. xv. p. 10.

Glucine is soluble in the fixed alkalis, but not in ammonia; it is dissolved, however, in carbonate of ammonia, forming a triple salt,—a property characteristic of it, though possessed also by zircon and ittria; it is also dissolved by the other alkaline carbonates. It decomposes the salts of alumina.

Glucine combines readily with the acids; its salts have a sweet taste: those of them which are soluble in water, (which the greater number are), are not crystallizable, but form by concentration viscous solutions. They are decomposed by the fixed alkalis, and the earth is completely precipitated from their solutions by ammonia. Infusion of galls throws down a precipitate of yellowish flocculi from some of these solutions, such as the acetate. Prussiate of potash gives a white precipitate. Neither oxalate of ammonia, nor tartrate of potash, causes any precipitation, but phosphate of soda does. The properties of the individual salts have been imperfectly determined.

Carbonate of Glucine, formed by precipitation from a salt of glucine, by the action of an alkaline carbonate, affords, when dried, a light white powder; it is insoluble in water, and is not rendered soluble by an excess of acid: it effervesces with the acids, but the effervescence does not immediately appear with the weaker acids, such as distilled vinegar, unless heat be applied: it is decomposed by heat, losing about 50 *per cent.*, but part of this loss, it is remarked by Vauquelin, must be owing to the expulsion of water.

Nitrate of Glucine is very soluble in water, and retains it so strongly that it cannot be crystallized: by evaporation it forms a gelatinous mass, which is not even easily dried, and which is very deliquescent. Its taste is sweet and astringent.

Sulphate of Glucine.—When sulphuric acid is digested on newly precipitated carbonate of glucine, the quantity of which is larger than the acid can dissolve, the portion which remains loses its pulverulent form and its opacity; it becomes liquid, viscous, and semi-transparent. This solution is partially decomposed by water, white flocculi being precipitated, which the acid added in a few drops re-dissolves. These flocculi, Vauquelin remarks, appear to be a sub-sulphate, though the liquor from which they are separated remains very slightly acid *. The neutral sulphate has a sweet and astringent taste; it is very soluble in water, and is difficultly crystallizable, the solution assuming, by evaporation, the consistence of a syrup. It is decomposed at a red heat.

PHOSPHATE OF GLUCINE, obtained by decomposing nitrate of glucine by phosphate of soda, is in the form of a viscous substance, insipid, and insoluble in water, but rendered soluble by an excess of acid. It is melted by heat into a transparent vitreous globule.

MURIATE OF GLUCINE is very soluble in water; and by evaporation can be obtained in small crystals.

FLUATE OF GLUCINE may be prepared by mixing together fluate of potash slightly acidulous, and muriate of glucine sensibly acid. The fluate of glucine is thrown down in a gelatinous precipitate: it may be dissolved in hot water, and on cooling affords small crystals. The peculiarity has been already pointed out under the general history of the fluates; that alkalinity is produced in its formation by double decomposition, without correspondent acidity in the fluate.

In its solubility in potash and soda, as well as in some other of its properties, glucine resembles alumina; and in the sweet taste of its salts, and being soluble in carbonate of ammonia, it bears a resemblance to ittria. These analogies led Vauquelin to undertake a more minute examination of it, with a view to discover if it did not derive its characters from some intermixture or modification of these earths: but he found every reason to conclude, that it is

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* Annales d'Histoire Naturelle, tom. xv. p. 12.

unconnected with either, and is a substance essentially distinct. Its affords no trace of alum from the addition of potash to its solution in sulphuric acid; and it is farther distinguished from alumina, by the saccharine taste of its salts, by its solubility in carbonate of ammonia, and by exerting stronger attractions to the acids. It differs from ittria in not forming crystallizable salts, in being soluble in the fixed alkalis, and in not being precipitated by oxalate of ammonia, or by tartrate or citrate of potash *.

CHAP. IX.

OF ITTRIA.

This earth was discovered by Gadolin, a Swedish chemist, in a fossil found at Ytterby in Sweden, in which it is combined with silica, lime, and iron †. The discovery was confirmed by Ekeberg, Klaproth, and Vauquelin: the same earth has been discovered in some other fossils, combined with the newly discovered metal, tantalum. It resembles glucine in some of its properties, but differs entirely in others. Its great specific gravity, and its being precipitated by the alkaline prussiates, and by tannin, from its solutions, in some measure connect it with the common metals. It is not reduced, however, to the metallic state by heating it with charcoal, but it runs with it into a kind of semi-fluid mass, which is heavier than the earth.

The process followed by Vauquelin to obtain the earth

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* Annales d'Histoire Naturelle, tom. xv. p. 14, 18.

† Journal des Mines, tom. xii. p. 247. Annales de Chimie, tom. xxxvi. xxxvii.

from the gadolinite, the first of these minerals, was to dissolve it with the assistance of heat in diluted nitric acid, pouring off the solution from the undissolved silica. The liquor is then evaporated to dryness, by which any remaining silica, and any oxide of iron, are separated from combination with the acid. By re-dissolving the residuum in water, the compound of nitric acid and ittria is obtained: if there are any traces of iron, the liquor is either again evaporated to dryness, or a little ammonia is added; and after the separation of the oxide of iron in yellow flakes, the solution is decomposed by ammonia, which precipitates the earth *. The process employed by Klaproth is similar; nitro-muriatic acid being employed; the iron being removed by the action of succinate of soda; and the ittria being precipitated by carbonate of soda †. In a subsequent process employed by Vauquelin, he employed sulphuric acid diluted to dissolve the gadolinite instead of nitric; abstracted the iron from the sulphate by long continued calcination at a red heat, repeating this, if necessary, after lixiviation a second time, and when the solution is of a very sweet and astringent taste, and retains only a light rose colour, precipitating any remaining metallic matter, by adding cautiously small quantities of hydro-sulphuret of potash, as long as any coloured precipitate is formed: from the clear liquor, ittria is then precipitated by the addition of ammonia ‡. According to Berzelius, oxide of cerium is a constituent ingredient of gadolinite; and the ittria obtained by Gadolin and Ekeberg had not been procured free from this metallic oxide ||; a circumstance, he adds, not surprising, as the analogies between these substances are striking, and their distinctions not well marked. The best

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* Philosophical Magazine, vol. viii. p. 569.

† Analytical Essays, vol. ii. p. 47.

‡ Annales d'Histoire Naturelle, tom. xv. p. 16.

|| Annals of Philosophy, vol. vii. p. 60. viii. p. 256.

method of discovering the intermixture with it, is to expose it in an open crucible to a strong red heat; if cerium is present, the ittria assumes a brown colour; on dissolving it in concentrated nitric acid, the red or orange colour of the solution affords a farther indication of this metallic oxide; and, lastly, if after dilution with an equal volume of water, a small piece of sulphate of potash is added, and it causes, after some time, a precipitate of a white or light yellow colour, this is a proof of a triple sulphate of cerium. It is very difficult, Berzelius adds, to free completely the ittria from the oxide of cerium by re-agents, as both are precipitated together; and hence it is more easily obtained pure from the ittro-tantalite, than from the gadolinite. The best method he could discover, was to convert them into triple sulphates with potash, by adding sulphate of potash to the solution containing both; these have not the same degree of solubility; and in water impregnated with sulphate of potash, the triple sulphate of potash and cerium is scarcely dissolved. The sulphate of potash and ittria, which retains some portion of cerium, may be decomposed by ammonia; the precipitate being washed, is dissolved in nitric or muriatic acid; the solution is precipitated by sub-carbonate of ammonia added in large excess, to re-dissolve the ittria, leaving the oxide of cerium undissolved; and the clear liquor being heated, to expel the sub-carbonate of ammonia, the ittria is obtained pure *.

When ittria is submitted to the action of potassium at a high degree of heat, potash, according to Davy, is formed; and there are appearances of metallic particles intermingled with the potash. From the quantity of carbonic acid, and of sulphuric acid, which ittria saturates, Berzelius infers, on the principle already illustrated, that it is composed of 18.5 of oxygen, and 81.5 of base †; or, from

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* Annales de Chimie et Physique, tom. iii. p. 26. 35.

† Annals of Philosophy, vol. iii. p. 359.

a subsequent result, that it saturates an equal weight of sulphuric acid, of 20, and 80 of base *.

Ittria, when pure, is in the form of a powder perfectly white, and insipid: it is heavier than any other earth; its specific gravity, according to Ekeberg, being 4.84. It is not fusible alone, but with borax it melts and forms a white glass. It is not soluble in water; but in its precipitation from its solutions it combines with a portion of water, which it retains with considerable force. The quantity, according to Klaproth, amounts to 31 *per cent.*

Ittria is not dissolved by the liquid alkalis, nor, as Ekeberg found, do they redissolve it when added in excess, after having precipitated it from its solutions. This affords a distinguishing character between it and glucine. It is soluble in carbonate of ammonia, a property in which it resembles glucine, but it requires five or six times more of the carbonate for its solution than glucine does.

Ittria combines with the acids, and exerts affinities to them of considerable strength, as it precipitates alumina, glucine, and zircon, from their solutions; it is precipitated by the alkalis and the alkaline earths. Its salts have a sweet and astringent taste; several of them were supposed to be coloured, but this, Ekeberg shewed, arises from the presence of metallic matter,—oxides of manganese and iron, to which, according to the observations of Berzelius, is to be added cerium: when free from these they are colourless. Those of them which are soluble, the sulphate, nitrate, muriate, and acetate, are crystallizable; they are always acidulous, and even with this excess of acid refuse to dissolve any additional portion of earth; the insoluble salts,—the phosphate, carbonate, oxalate, tartrate, and citrate, are, on the contrary, obtained neutral †. From the insolubility of these latter compounds, the solutions of ittria are precipitated by phosphate of soda, carbonate of

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* Annales de Chimie et Physique, tom. v. p. 34.

† Vauquelin, Annales d' Histoire Naturelle, tom. xv. p. 18.

soda, oxalate of ammonia, and tartrate of potash. They are decomposed by the alkalis and the alkaline earths. Prussiate of potash throws down from their solutions a precipitate of a white or pearl grey colour, another property by which it is distinguished from glucine. It is also precipitated in grey flocculi by the watery or spirituous infusion of galls, but very slightly by pure gallic acid. It is not affected by sulphuretted hydrogen, or hydro-sulphuret of ammonia added to its saline solutions.

CARBONATE OF ITTRIA is precipitated from a solution of ittria by an alkaline carbonate, in the state of a white powder. Ittria itself, when newly precipitated by a caustic alkali, it is remarked by Vauquelin*, absorbs during its drying, from exposure to the atmosphere, a sufficient quantity of carbonic acid to become effervescent. The carbonate, he adds, is heavy, white, and opaque, and loses by calcination from 30 to 32 hundredths of carbonic acid and water.

NITRATE OF ITTRIA is very soluble, and can scarcely be crystallized: it assumes a gelatinous consistence by evaporation, and becomes brittle when this jelly cools. Its taste is sweet and astringent.

SULPHATE OF ITTRIA, formed by the action of the acid on the earth, crystallizes in small brilliant grains, of a rhomboidal form. Their taste is sweet and astringent. They require from 25 to 30 parts of water for their solution, and are not more soluble in hot water.

PHOSPHATE OF ITTRIA, formed by mixing solutions of phosphate of soda, and of a soluble salt of ittria, is insoluble, being thrown down in a gelatinous precipitate.

MURIATE OF ITTRIA is obtained by evaporation of the solution of the earth in muriatic acid, in a gelatinous form; it does not easily become dry, and it speedily deliquesces on exposure to the air; it melts with a gentle heat.

FLUATE OF ITTRIA.—This salt is formed by the same

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* Vauquelin, Annales d' Histoire Naturelle, tom. xv. p. 18.

process as the fluates of glucine and zircon, and like them, according to Gay Lussac, is precipitated neutral, and altogether insoluble in water, from an acidulous solution, though the corresponding salt arising from the double decomposition remains neutral *.

CHAP. X.

OF THORINA.

Berzelius, in submitting lately to analysis certain minerals found in the neighbourhood of Fahlun in Sweden, observed a substance to remain, possessed of properties which have led him to consider it as a new earth. The minerals in which it was discovered were a variety of Gadolinite, and what he has called the deuto-fluate of cerium, and the double fluate of cerium and ittria. He was not always able, however, to extract it from varieties of these minerals even apparently the same, and he obtained only a small quantity on which he was able to perform his experiments. Some doubt, therefore, may perhaps be entertained with regard to it; its properties at least cannot be considered as fully determined: and in his Memoir † he admits the imperfection of the notice with regard to it. As connected with the place of its discovery, he has given it the name of Thorina, from Thor the Scandinavian deity.

To obtain it from those minerals which contain protoxide of cerium and ittria, the oxide of iron is first to be

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* Recherches Physico-Chimiques, tom. ii. p. 29.

† Annales de Chimie et Physique, tom. v. p. 1. translated. Annals of Philosophy, vol. ix. p. 452.

separated by succinate of ammonia: the deutoxide of cerium is then precipitated by sulphate of potash; after which the ittria and the new earth are precipitated together by caustic ammonia. They are to be dissolved in muriatic acid; the solution is to be evaporated to dryness, and boiling water is poured on the mass, which dissolves the greater part of the ittria. The residue contains, however, still a portion of ittria. It is to be dissolved in muriatic or nitric acid, and evaporated, so as to attain neutralization as exactly as possible; water is then to be poured upon it, and boiled for an instant. The new earth is precipitated, and the liquor contains free acid. In again saturating it, and boiling the solution, a precipitate of the earth is obtained.

Collected on a filtre, it presents a gelatinous semi-transparent mass. Washed and dried it becomes white, absorbs carbonic acid, and re-dissolves in acids with effervescence. Heated to redness it retains its white colour; if it has been exposed only to a moderate heat, it dissolves easily in muriatic acid; but if calcined more strongly, it does not dissolve but with the heat of boiling water in the concentrated acid. The solution is yellowish, but diluted with water it becomes colourless, as happens usually with glucine, ittria, and alumina.

It does not melt before the flame of the blowpipe, but it enters into fusion with borax, and forms a transparent glass, which, when exposed anew to the exterior flame, becomes milky and opaque. With phosphate of soda and ammonia it forms a transparent pearl. It does not melt with soda.

When this earth is newly precipitated, potash and caustic ammonia exert no sensible action on it even at the heat of boiling water. The solutions of the carbonates of these alkalis dissolve a small portion of it, which is again precipitated when the liquor is saturated with an acid, and neutralized by caustic ammonia. It is much less soluble in the alkaline carbonates, than any of those earths formerly known to be dissolved by them.

Thorina combines with facility with the different acids. Its neutral solutions have a taste purely astringent, which is neither saccharine, saline, bitter, nor metallic; in which respect it differs from all the earths except zircon.

Dissolved in Sulphuric Acid with a slight excess of acid, and submitted to evaporation, it forms readily transparent crystals, which do not alter in the air, and the taste of which is strongly astringent. These appear to be the neutral SULPHATE. The acidulous residual liquor after their formation retains little of the earth. When submitted to the action of water, they are slowly decomposed, a sulphate with excess of base precipitates, and a super-sulphate remains in solution. If agitation has been avoided, the portion not dissolved with excess of base retains the form of crystals, but the least motion reduces them to powder. The acidulous sulphate mixed with sulphate of potash even to saturation, gives no precipitate; neither is any produced when sulphate of potash is added to the muriate.

When newly precipitated, it dissolves very easily in Nitric Acid; but if it has been previously calcined at a red heat, it requires to be boiled in the acid to be dissolved. The solution does not crystallize, but produces a gummy mass, which left exposed to the air becomes more liquid, and which, evaporated by the heat of a sand-bath, affords a white opaque matter, similar to enamel, nearly insoluble in water. The solution of the nitrate in water is a neutral compound, which is decomposed by boiling, the greater part of its earth being precipitated; and even the solutions with a slight excess of acid give a deposite of it, if diluted and heated to ebullition.

It dissolves in Muriatic acid in nearly the same manner as in the nitric. The solution does not crystallize: evaporated at a moderate heat, it is converted into a syrupy mass, which exposed to the air is not deliquescent, but, on the contrary, dries, becomes white, similar to enamel, and does not dissolve in water but in very small quantity, leaving a salt with excess of base, so that, by spontaneous evaporation, it appears to give out the portion of muriatic acid which renders it soluble in water. A solution which has not too great an excess of acid, when diluted and made to boil, deposites the greater part of the earth in a gelatinous form. The property which a solution of this earth in muriatic or nitric acid has, of leaving on the sides of the vessel, when it is evaporated at a strong heat, a white and opaque layer, similar to enamel, which appears, in particular, very easily when the solution has been spread over the vessel, is a very characteristic one, and serves to detect its presence.

Thorina combines with avidity with Carbonic Acid. When precipitated from its solutions, it absorbs in drying carbonic acid from the air. And the alkaline carbonates precipitate it with the whole of their carbonic acid.

Oxalate of ammonia throws down a white bulky precipitate, insoluble in water, or in caustic alkaline solutions.

Tartrate of ammonia produces a white precipitate, which is re-dissolved, and does not become permanent until a sufficient quantity of that salt has been added. The precipitate is dissolved by caustic ammonia.

Citrate of ammonia gives no precipitate, not even when caustic ammonia is added; but if the liquor is heated to boiling, the earth is precipitated as the ammonia evaporates.

Benzoate of ammonia produces a white bulky precipitate.

Succinate of ammonia causes a precipitate to form, which is speedily re-dissolved.

Ferro-prussiate of potash gives a white precipitate, which dissolves completely in muriatic acid.

A portion of this earth was exposed in a charcoal crucible, to the degree of heat employed to reduce tantalum, and was kept at this for an hour. It appeared to suffer no other alteration than having contracted, and acquired a little transparency, probably from imperfect fusion. There was no appearance of reduction, and it dissolved by boiling in muriatic acid. As it is now admitted that the salifiable bases are metallic oxides, it may appear indifferent, Berzelius remarks, whether a substance be designated an earth, or an oxide of a metal. But, as he justly adds, since these bodies are divided into alkalis, earths, and metallic oxides, it appears the just method to attach each new link of the chain of oxides to those with which it has the greatest analogy; and as the earths are distinguished particularly by the property of being colourless, and of not being reduced by charcoal, without the aid of another metal, thorina may be considered as belonging to the class of earths.

Berzelius adds the following enumeration of its differences in properties from those other earths to which it has the greatest resemblance. From alumina it differs by its insolubility in caustic potash,—from glucine by the same property,—from ittria by the taste purely astringent, and not sweet, of its salts, and by its solutions, when they have not too great an excess of acid, being precipitated by boiling,—and from zircon, in being capable of being dissolved by acids after calcination at a red heat; in the sulphate of potash not precipitating its solutions, while it precipitates zircon even from very acid solutions; in being precipitated by oxalate of ammonia, which zircon is not; and in its sulphate crystallizing easily, while that of zircon, if free from alkali, forms on drying a viscous transparent mass, in which there is no sign of crystallization. Zircon, however, is on the whole the earth to which it has the greatest analogy, and it deserves remark, that both these earths are found together.

BOOK VI.

OF METALS AND THEIR COMBINATIONS.

THE METALS form an extensive class of substances, important in their chemical relations, and in the numerous uses to which they are applied. Excluding the bases of the alkalis and earths, which, although probably of a metallic nature, are still so far peculiar, that it would be improper to place them at present under the class, they amount to about twenty-eight; the greater number of which are of modern discovery. They are all simple; they have not only not been decomposed, but there are no grounds, from any analogy, to regard them as compounds.

In strict definition, the metals are inflammable bodies; they combine with oxygen, and many of them, during this combination, exhibit the phenomena of combustion. But they are distinguished from other inflammables, and from all other classes of chemical agents, by very appropriate qualities,—great specific gravity, considerable tenacity and hardness, opacity, and a peculiar lustre or brilliancy.

Of these properties of the metals, none is more characteristic than their great density and consequent superior specific gravity. In this they exceed all other bodies, some having a specific gravity, compared with water, as 18 or 20 to 1, and the lightest being above 6. If the bases of the alkalis are to be admitted as pure metals, this property could not be regarded as distinctive, as they are even lighter than water; but the levity of these substances, it has already been stated, may be owing to the presence of hydrogen, combined with their metallic matter.

Opacity is another property characteristic of the metals. They transmit no light, even when reduced to the greatest tenuity. Gold leaf, however, beat to the greatest thinness of which it is susceptible, transmits a green light, which has been supposed owing to minute fissures, through which the light in passing suffers refraction; but such fissures ought to occur in the other metals beat to their state of greatest tenuity; and the cause why light is capable of being transmitted only through gold, is that from its greater malleability it can be reduced to finer leaves.

From the conjunction of these qualities, density and opacity, arises another characteristic property of the metals,—lustre or brilliancy. By their opacity, and the denseness or closeness of their texture, they are enabled to reflect the greater part of the light that falls upon their surface. From their density they are susceptible of a high polish, by which their lustre is increased.

Tenacity, or the strong cohesion of their particles, distinguishes a number of the metals, and is not possessed in any great degree by other bodies. It gives rise to two properties, Malleability and Ductility, analogous, but still distinct. Malleability is that property from which they may be beat or pressed into fine plates or leaves; ductility, that by which they may be drawn into fine wire. The reducing them into thin leaves is performed, either by a strong and uniform pressure applied by a roller, or by beating with a hammer. The extension into fine wire is done by drawing the metal formed into a cylinder through conical holes in a metalline plate, the wire being drawn successively through holes of smaller diameter. In either of these operations, the metal is liable to become rigid, so as to break when it is reduced to a certain degree of tenuity. This is remedied by annealing it, or heating it, and allowing it to cool slowly; it thus becomes capable of farther extension.

Though the malleability and ductility of metals are connected, they are not always in the same proportion. Gold is most malleable, but in ductility is inferior to iron, platina, silver, and copper. Iron exceeds the others in ductility, but is scarcely malleable. Tin and lead have malleability, but little ductility. Some of the metals are neither malleable nor ductile: these were named Semi-metals;—an improper distinction, now disregarded.

The cause of the tenacity of metals, whether malleability or ductility, has been supposed to be a peculiar state of their particles in relation to the force of cohesion, allowing them to move with regard to each other, without passing the limits at which this force is exerted. The difference between ductility and malleability has been ascribed to the figure and arrangement of their particles. The malleable metals may be conceived to consist of small plates, and the ductile metals of minute fibres, placed beside or over each other; the one slide by their flat surfaces, the other lengthen and exert an adhesion from one extremity to the other. The two properties appear to be connected with the state with regard to softness. In the metals which have much hardness, this quality opposes a resistance to their extension into leaves; and hence tenacity in these appears under the form of ductility; iron and platina are accordingly the metals which can be drawn into the finest wire. In the softer metals, again, as gold, tin, and lead, the extension into fine wire is difficult, while they can be beat into thin leaves. The property of tenacity, under either form, is considerably dependent, as has been remarked, on the state of aggregation produced by temperature, and by its slow or rapid reduction. It is singular that it is liable to be changed by other causes, not so obviously affecting the arrangement of the parts. Brass becomes brittle from exposure to a damp atmosphere, and steel changes its state of elasticity by friction at the surface.

In Hardness the metals are surpassed by the diamond, and some earthy fossils. Still some of them, such as platina and iron, are considerably hard. Their elasticity follows the same order as their hardness. Both qualities are increased, by heating the metal and suddenly cooling it, and by hammering. The tenacity and softness are restored by heating the metal, and allowing it to cool gradually, changes evidently connected with the state of aggregation.

Metals, in their relation to caloric, have some peculiarities. They are the best conductors of this power. Their expansibilities are various, and seem to be nearly in the order of their fusibilities. With regard to fusibility, they differ greatly. Mercury is fusible at so low a temperature, that it becomes solid only at 40° below the commencement of Fahrenheit's scale; others, as platina or molybdena, can scarcely be melted at the most intense heat; and between these extremes is a series in which the degrees of fusibility are very various. A metal in its melted state retains the qualities of opacity and brilliancy, and the lustre is even greater, as the surface is perfectly smooth. In congealing, some metals expand, especially iron, bismuth, and perhaps antimony. All the others, according to the experiments of Reaumur, contract; and the contraction of some of them is very considerable: that of mercury is equal, according to Cavendish, to $\frac{1}{23}$ of its volume.

In congealing, a crystalline arrangement, more or less obvious in the fracture of the metal, is assumed; and by particular management, a number of the metals may be regularly crystallized,—the melted metal being allowed to cool slowly, and, when the mass has become solid at the surface, the thin crust being pierced, to allow the internal liquid part to run out. The internal surface exhibits crystals, which in the different metals are nearly of the same figure, that of a pyramid, single or double, of four sides; or in some, as zinc, that of a prism *.

The metals are volatilized by heat. Quicksilver boils at a temperature of 660°; zinc and arsenic rise in vapour at a temperature not very remote from this; and a number of the others are dissipated in vapour in the intense heat excited in the focus of a large burning mirror, or by a powerful galvanic discharge.

A distinguishing property of metallic bodies is that of generating electricity by mutual contact, especially when certain chemical agents are likewise placed in the series. They are also the best conductors of electricity.

Metals are very susceptible of combination: they exert affinities to oxygen, to hydrogen, carbon, sulphur, phosphorus, and to each other; and when combined with oxygen, to the acids, the alkalis, and the earths. On these combinations, some general observations are to be stated, previous to the history of the individual metals.

Their combinations with oxygen are the most important. When a metal is exposed to heat, with the access of atmospheric air, it begins to suffer an evident change, more or less rapid in different metals: its surface becomes dull; the metallic lustre is at length lost; and if the metal suffer this change while solid, thin scales form on its surface; if it be in fusion, its surface is covered with a powder. On removing this, the metal beneath is bright, but it continues to undergo the same change, and thus the whole of it may be successively converted into this new product.

This process was by the older chemists named Calcination, and the product was called a Metallic Calx. The phenomena were explained in conformity to the theory of Stahl. Metals having an evident relation to inflammable bodies, and some of them in the above process exhibiting

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* Journal de Physique, 1781, p. 74.

phenomena analogous to those of combustion, they were supposed to contain phlogiston, or the common principle of inflammability, combined in each with a peculiar base. During calcination, Stahl supposed the phlogiston to be expelled, and the earthy-like powder which remained, or the calx, to be the base with which it had been combined. Hence, what was regarded as a confirmation of this explanation, if a metallic calx were exposed to heat, mixed with a portion of inflammable matter, it was found to be reduced to the metallic state; the phlogiston being transferred, as was supposed, from the inflammable body to the metallic base, and forming the metal.

One obvious objection to this theory was, that it did not account for the necessity of the presence of the atmospheric air to metallic calcination. And another fact, equally conclusive against it, was, that the metal by calcination increased in weight; 100 lbs. of lead, for example, affording 110 lbs. of calx.

The fallacy of the hypothesis was at length demonstrated by Lavoisier and Bayen. The former chemist, led by his general views with regard to the theory of Stahl, to ascribe metallic calcination to the absorption of a part of the air, advanced this opinion in a memoir read before the Academy of Sciences, and published in 1774; and supported it by urging the fact of increase of weight in metallic calces, compared with the metals from which they are formed; by shewing that metallic calcination requires the presence of air, which during the process suffers a diminution of volume; and by ascertaining, that when the calx is reduced, by heating it with charcoal, to the metallic state, a large quantity of air is disengaged. Bayen had about the same time been engaged in similar researches, particularly on the calces which are precipitated from solutions of the metals in acids. He shewed that the weight of these was greater than that of the metal dissolved, and inferred, that although part of this weight was owing frequently to a portion of the acid, by which the metal had been dissolved, adhering to the precipitate, it was also in part owing, adopting an expression employed by Lavoisier, to an elastic fluid fixed in the metal. To prove this, he examined accurately the phenomena which occur in the reduction of these precipitates. He found, that when reduced, by heating them with charcoal, much elastic fluid is disengaged; and what afforded the most direct demonstration of the theory, he succeeded in reducing some of these calces, particularly those of mercury, by heat alone, and obtained a large quantity of air during the reduction*. Priestley afterwards discovered, that the air obtained by heat from calcined mercury is oxygen; and the discovery of this gas enabled Lavoisier to complete the theory of metallic calcination, which he now ascribed to the combination of the metal with oxygen. This he established by a series of extensive and accurate experiments. He proved, that the calcination of a metal cannot proceed without the presence of oxygen; that the oxygen present disappears; that the weight which the metal uniformly gains in its calcination, is equal to the weight of the oxygen which is consumed; and that this oxygen can again be obtained from the calx, which returns to the metallic state; in some cases, by the operation of heat alone, when the oxygen is obtained pure; in others, by heating it with an inflammable substance, with which the oxygen combines affording the known product of such a combination. The old terms of Calx and Calcination were discarded, as conveying erroneous ideas, and were succeeded by those of Metallic Oxide, and Metallic Oxidation.

Metals, in suffering oxidation by exposure to heat and atmospheric air, in general combine slowly with the oxygen of the air: they do not render sensible much heat or light, and therefore do not present the appearances of com-

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* Journal de Physique, 1774.

bustion. In some, however, the oxidation is more rapid, and is accompanied with a vivid combustion, as in the example of zinc; and if the temperature be raised much above that which is requisite to the slow calcination, the combination in all of them is accompanied with an evolution of light. Thus tin burns at a high heat with a white light, antimony with a yellow, and copper with a green light. Iron in oxygen gas burns with great splendour: and by the intense heat excited by a powerful galvanic apparatus, even gold and silver may be made to undergo combustion.

The facility of oxidation of the metals is regulated by various circumstances. It depends not merely on their affinity to oxygen; but on this modified principally by their cohesion; and therefore by their fusibility and volatility.

The force of cohesion being considerable in the metals, few of them are susceptible of oxidation but at a high temperature. A number of them require to be in fusion to admit of the combination. Some, however, as iron and copper, are oxidated when exposed to a heat, much inferior to that which melts them; their surface is slowly tinged with various colours, and at length scales of oxide are formed. Even when in fusion, several require the cohesion to be farther diminished by the operation of caloric, to enable them to attract oxygen; and some, as antimony and quicksilver, must be raised to their vaporific point. Gold, silver, and platina, can scarcely be directly combined with oxygen; and hence, suffering no change when exposed to very intense heats, they were formerly named Indestructible Metals. The reason is, not that they have no affinity to oxygen, for we can combine them with it by indirect methods; but that, having much cohesion, and an affinity comparatively weak, this cohesion resists the combination, and when heat is applied to overcome it, the elasticity of the oxygen gas is augmented, while the attraction is not sufficiently powerful to enable them to fix it. But if the cohesion be weakened without raising the temperature, as by dissolving them in quicksilver, their oxidation may be effected; as it is also, if a very intense heat be suddenly applied. Hence their oxidation, by a powerful electric discharge, as shewn in the experiments on the oxidation of metals by electricity by Mr Cuthbertson *, and their combustion when exposed to the action of a galvanic battery.

It is not easy to assign the order of the affinities of the metals to oxygen, from the difficulty of appreciating the effect of the circumstances by which their combination is influenced. Judging from the comparative difficulty or facility of decomposition, manganese, molybdena, iron, and zinc, have the most powerful attraction towards it, as their oxides are decomposed with difficulty by charcoal, assisted by a high heat. The oxides of copper, lead, bismuth, and arsenic, are reduced to the metallic state by the agency of hydrogen. And the oxides of quicksilver, silver, and gold, are decomposed by heat alone, denoting a weak affinity. The different metals too combine with different quantities of oxygen, which, according to Berthollet's theory, may be considered as indicating the order of attraction; and the order thus indicated, agrees in general with that inferred from the difficulty of decomposition. 100 parts of the perfect oxide of manganese, contain 40 of oxygen, of that of iron 33, of tin 28, of lead 21, of copper 20, of bismuth 17, of quicksilver and silver not more than 10 parts.

Each metal combines in general with more than one proportion of oxygen, and from these different degrees of oxidation, compounds distinguished by very various properties are formed.

It was an opinion generally received, that these combinations of a metal with oxygen, take place in determinate proportions, and that there are no intermediate combinations. Thus there are two oxides of iron, one of a black,

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* Nicholson's Journal, 4to, vol. v. p. 156.

and another of a red colour, the former containing 21 of oxygen in 100 parts, the other 33; and the oxidation of iron was supposed to be confined to these two proportions. In like manner, there were supposed to be only two oxides of gold, a purple and a yellow; two oxides of manganese, a white and a black; and, in general, two degrees of oxidation of each metal. This opinion was in particular maintained by Proust*. Others, as Thenard†, suppose that there may be more than two oxides of the same metal, but that the combination is in determinate proportions. The opposite opinion was advanced by Berthollet. He maintained, that the proportions may vary progressively from the term at which the combination of the metal with oxygen becomes possible, to that at which it acquires the highest degree of oxidation; that in many cases it does so; and that if, in others, determinate proportions are observed, this is owing to the operation of circumstances, which, at these proportions, limit the combination, and which in general being uniform, give rise to an invariable proportion‡.

In support of his opinion, Berthollet reviewed a number of facts connected with metallic oxidation. In the decomposition, for example, of a metallic oxide by heat, there is often apparently a mere progressive reduction in the state of oxidation, without any marked transition from one definite compound to another. The black oxide of manganese contains the metal at the maximum of oxidation; it is decomposed by heat, more or less, according to the intensity of the heat applied; it thus passes through different shades of colour, from black to brown, and different quantities of oxygen are expelled without any apparent limitation of proportions. He farther shewed ||, that metals

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* Journal de Physique, tom. lix. p. 521.

† Annales de Chimie, tom. lvi.

‡ Chemical Statics, vol. ii. p. 316.

|| Journal de Physique, tom. lxi.

may be made to pass through degrees of oxidation so numerous, and with transitions so imperceptible, as to prove apparently that they are indefinite, or nearly so.

If melted tin, he remarks, be exposed to the air, it is covered with a blackish pellicle, which is the metal in the first degree of oxidation; from this any metallic tin may be abstracted by washing, and it then dissolves partially in muriatic acid, hydrogen being disengaged. If this oxide be exposed to a red heat, there is an appearance of inflammation, and after being stirred for some time under exposure to the air, it becomes of a light grey colour, and forms an oxide which dissolves in muriatic acid, without any disengagement of hydrogen. If exposed to a stronger heat, it again becomes luminous, and after this is of a light grey colour: if the heat be still farther raised, the same luminous appearance is observed, and the colour of the oxide becomes of a still lighter grey. This again, when urged with a more intense heat, becomes of a white colour with a shade of grey. If, instead of following this process, tin be exposed at once to a very high degree of heat, or if it be deflagrated with nitre, it gives a vivid light, and is converted into a white oxide. Lastly, if the metal be oxidated by nitric acid, and afterwards exposed to heat, it gives a product of a yellow colour, which appears to be the oxide at the maximum. There are thus not less than seven degrees of oxidation in tin, or, avoiding every ambiguity, at least five. Four degrees of oxidation have been observed in lead. The number of the oxides of iron is not easily determined; some have supposed four, others seven, and in those of them which occur in nature crystallized, a distinct crystalline form is observed, establishing sufficiently their specific distinctions, while by analysis they yield only iron and oxygen. And since in all these examples, the degrees of oxidation are so numerous, there is reason to suppose that they are not determinate, but indefinite, and that by varying the temperature or other external circumstances, the number may be increased. He lastly shewed, that external forces might insulate a combination at certain proportions; and thus give rise to uniform and definite compounds. The fusion of a metal affords an example of this. If it be oxidated at the point at which it melts, as that point is not variable, the oxide will be uniform, or one determinate proportion will be observed in the combination: for the same reason, the oxide formed at the vaporific point of a metal will be always the same: and the affinities of acids may also determine the oxidation, by being exerted more powerfully to the metal in one degree of oxidation than another.

In opposition to these arguments, the consideration was chiefly urged, that definite proportions are established in chemical combinations where powerful affinities operate, and therefore they may be expected to occur in metallic oxidation. And the results apparently adverse to this in the production of oxides of numerous and indeterminate degrees of oxidation, were accounted for by supposing such products to be *mixtures* of oxides of definite composition.

It is obvious, that this is merely a part of the general question, whether definite proportions are established in chemical combination, which has been already fully considered under the general doctrines of attraction. Berthollet's views appear to accord with a number of facts. But still the principle is proved, that definite proportions are established from the immediate exertion of chemical attraction. And the law demonstrating this more clearly with regard to other compounds, appears also to exist with regard to the combination of metals with oxygen,—that the higher proportion of one of the ingredients is a simple multiple of the lower. Taking the metal in a fixed quantity, and considering the oxygen combined with it in different proportions, these proportions, when we select the cases in which there is least ambiguity, and in which the oxides are best defined, appear to have simple arithmetical ratios. Thus 100 of quicksilver combine in the first oxide with 4 of oxygen, and in the second with 8 : 100 of copper combine with 12.5 in the first, and 25 in the second. Now this is a result, which, as has already been remarked with regard to analogous cases, cannot be accounted for on the supposition of proportions being established by the operation of external forces; but must be admitted as a proof, that the mutual attraction is more forcibly exerted in these proportions than in others; and that hence they are established by its immediate exertion.

There is some uncertainty, however, attached to this subject from the opposite class of facts proving at least numerous degrees of oxidation, to which perhaps due weight has not been allowed. They are not well accounted for on the hypothetical assumption of mechanical intermixture being present in these cases which do not come under the law; for since the whole quantity is operated on under the same circumstances, there is no cause to establish a different degree of oxidation in one part of it from what is in the other. In the decomposition, for example, of the black oxide of manganese by heat, in some of the intermediate stages of the decomposition, the product is supposed to be a mixture of two definite oxides; yet why, since the whole is at the same temperature, should it not be reduced to the same extent, or how can these different oxides, one of which is reducible farther, exist together? Though the combinations of metals with oxygen are definite, they are in all probability more numerous than have been supposed; and although some proportions are more easily established than others, so that these usually appear, others may be effected by peculiar circumstances under which the combination takes place.

From the various degrees of oxidation of which metals are susceptible, it is necessary to have a precise nomenclature by which the distinction shall be expressed. But this is attended with considerable difficulty. The method usually employed has been to distinguish them from colour; hence the introduction of the terms grey oxide of mercury, red oxide of lead, &c. This, however, is rather vague; it has even been supposed that different oxides of the same metal are in some cases of the same colour; though of this there is reason to doubt. Still, if a nomenclature could be applied expressing the series of oxidation, it would be systematic and precise; but the difficulty with regard to this is, that it can only be properly applied when the series is perfectly fixed, and that if any uncertainty exist with regard to this, it would be to introduce a source of error, which, in the progress of the science, must be productive of confusion, since the discovery of a new degree of oxidation of a metal might render it necessary to change the whole series of names of its oxides. This forms the only objection to a mode of nomenclature proposed by Dr Thomson, otherwise extremely convenient, that of prefixing syllables derived from the Greek numerals, as *prot-oxide*, to denote the oxide in the first degree of oxidation, *deut-oxide*, that in the second, *trit-oxide*, that in the third, and *per-oxide*, to denote that in the highest state of oxidation. These terms may, however, be employed to express in the abstract, the oxides at these degrees of oxidation, though, to denote them specifically, it will in general be preferable to express them by some fixed distinction. That of colour is the most striking, and the most uniformly varied in the different oxides; though, should the distinction from it be in any case ambiguous, it may be drawn from some other quality which may not have this disadvantage.

In their general properties, the metallic oxides have a considerable resemblance. They are destitute of metallic lustre, opacity, and gravity, and have an earthy appearance: are uninflammable: generally tasteless, and insoluble in water: they are often fusible, and form coloured glasses more or less transparent, and often of dark colours; they exert affinities to the acids, the alkalis, and earths and in their combinations with the acids neutralize the acid properties. In their general relations they are analogous to the alkalis and earths; and in strictness of arrangement, as has been remarked, form with them perhaps only one class. They differ, however, from the alkalis, and from several of the earths, in being less soluble in water, whence they display less energy in chemical action; and there are other subordinate distinctions between them, which have been already pointed out.

Though usually insoluble in water, many of the metallic oxides appear, in common with the fixed alkalis and earths, to retain water in intimate combination, forming Hydrates. These combinations are established, when they are precipitated from their solutions in acids by an alkali; the quantity of water retained is frequently considerable, and modifies the properties of the oxide, particularly the colour. This water, however, it is not improbable, exists rather in the state of its elements, combined with the oxygen and metal of the oxide, conformable to the view which I have applied to the constitution of the alkalis and earths, though, in general, it is more easily expelled, leaving the binary oxide.

There are some metals capable of being so highly oxidated, as to pass to the acid state; such are arsenic, molybdena, chrome, and perhaps tungsten.

The process by which the metallic oxides are decomposed, and the metal recovered in its original state, is named in chemical language Reduction.

Some are reduced by exposure to heat; as the oxides of gold, silver, and quicksilver. Their oxygen is expelled at the temperature of ignition, and the metal returns to the metallic form. With regard to others, the decomposition by heat is partial, part of the oxygen is expelled, but the remainder is held in combination by a force of attraction which the heat, even though raised to a high degree of intensity, cannot overcome. Others are not decomposed but by the operation of other affinities. Hydrogen abstracts oxygen from some of these compounds, when the oxide is placed in hydrogen gas, and an elevation of temperature produced by the concentrated solar rays. Charcoal, or some carbonaceous substance, is more powerful; it is also more convenient in its operation; it is therefore generally employed as the medium of metallic reduction, and is capable of reducing the oxide of every metal.

In practical chemistry, some other substances are added which favour the reduction, principally by promoting the fusion of the metallic oxide, and thus facilitating the action of the charcoal upon it. On a large scale, lime is employed: in experiments on a small scale, potash is used under the form of what is named the Black Flux. This is prepared by exposing to heat, in an ignited crucible, a mixture of one part of nitrate of potash, with two parts of the crude tartar of commerce,—an impure tartrate of potash. The product consists of sub-carbonate of potash and charcoal, the carbonaceous matter being derived from the decomposition of the tartaric acid, of which carbon is an element. Equal parts of this black flux, and of the oxide intended to be reduced, are mixed together. The charcoal attracts the oxygen of the oxide, forming either carbonic acid or carbonic oxide: the first being chiefly produced when the metal has a weak attraction to oxygen, the second where the attraction is stronger; and the metal is melted as it returns to the metallic form. Vauquelin has observed, that in some cases the metal reduced in this mode gives traces of containing a small portion of potassium *.

Besides the oxidation of metals by the action of oxygen in its elastic form, they can be subjected to the same change by substances containing oxygen, and which im-

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* Annals of Philosophy, vol. xii. p. 16.

part it to them. They are thus oxidated by nitrate of potash, oxymuriate of potash, by acids, and by water.

The oxidation by nitre is effected only at a high temperature. The nitric acid of the nitre is decomposed, and part of its oxygen is attracted by the metal, so as to form generally that oxide in which the metal is at the maximum of oxidation: and with this the potash sometimes combines. Even those metals which are combined with oxygen with most difficulty, gold, silver, and platina, may be oxidated in this manner, as was known to the older chemists, and as has been established by Mr Tennant *.

The oxidation of metals by oxymuriate of potash, is effected by percussion, without the aid of heat, and is so rapid as to be attended with detonation.

Several of the metals receive oxygen from water, but the process, at a low temperature, goes on slowly. If iron-filings, moistened with water, be placed over quicksilver in a close vessel, the metal is oxidated, and hydrogen is evolved. At the temperature of ignition, this decomposition of the water and oxidation of the metal proceed with rapidity. Besides iron, zinc, manganese, and perhaps antimony, suffer it.

Acids are active in oxidating the metals, partly from yielding oxygen with facility, and partly from the attraction which the acid exerts. These actions present striking, and rather complicated phenomena, and from this, as well as from their importance, require some details.

Acids oxidate metals, either by directly affording to them oxygen, or by enabling them to attract it from water, or in some cases from the atmospheric air.

Nitric acid acts in the first of these modes; when poured on a metal, it is generally decomposed with rapidity, and by different metals, with different degrees of energy; nitric oxide, nitrous oxide, or even nitrogen, being evolved in the

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* Philosophical Transactions, 1797.

elastic form. A circumstance apparently singular, attending these actions, and of which a satisfactory explanation has not been given, is, that if the acid be concentrated, it is not decomposed by some of the metals, by tin, silver, or quicksilver, for example; but if a little water be added, or if the acid has been previously a little diluted, the decomposition proceeds rapidly. It is to be explained, I believe, on this principle,—that metallic oxides, like the alkalis and earths, combine with acids with most facility when in the state of hydrates; there must therefore be a sufficient portion of water, not essential to the constitution of the acid, to afford this; the result is thus perfectly similar to that already illustrated with regard to carbonate of barytes not being acted on by muriatic acid unless water be added. It is not evident, in the case of metals, with other acids than the nitric, because they are either not decomposed without heat, as in the example of the sulphuric, or sufficient water is present, as in that of the muriatic. It is not improbable, from this fact, that in all cases the metallic oxides combine, in the state of what are called hydrates, with the acid. When the metal is acted on by the acid, the oxide will pass into that state as it is formed, and when the metal previously oxidated is acted on, the acid by its action will enable the oxide to assume the same state.

Few of the metals are capable of attracting oxygen from the sulphuric acid, unless assisted by a high temperature. When aided by a sufficient heat, iron, zinc, copper, tin, quicksilver, and others, are oxidated by it. The phosphoric acid is of more difficult decomposition, and hence acts with less energy on the metals.

In other cases, the metal is oxidated by the acid enabling it to decompose the water present. This is exemplified in the action of sulphuric acid, which in its concentrated state has little effect on those metals which have even the strongest attraction to oxygen, as zinc or iron; but if diluted with water, the action is rapid, and attended with the copious evolution of hydrogen gas from the decomposition of the water. It is only in this way, too, that muriatic acid or fluoric acid acts on the metals: while nitric acid is so easy of decomposition, that it is always decomposed, and the metal receives oxygen from it alone; sometimes, however, with a decomposition of water at the same time, so that the nitrogen of the acid and hydrogen of the water being presented to each other in their nascent state, form ammonia, as has been already noticed.

The agency of an acid in promoting the decomposition of water, is owing, as has been before explained, to the affinity it exerts to the metal and oxygen, which concurring with the affinity of the metal to oxygen, these forces overcome the single affinity of the oxygen and hydrogen, and unite the metal, the oxygen, and the acid, in one combination.

Lastly, acids enable metals to combine with oxygen in the elastic form, or to attract it from the atmosphere. This happens with those metals which have a weak attraction to oxygen, and those acids the action of which is not energetic, as in the example of lead or copper, acted on by the acetic acid. If the air is excluded, they are not dissolved by this acid; but if partially immersed in it, and exposed to the atmosphere, the metal is oxidated, and dissolved at the surface, where it is exposed to the joint action of the acid and the air. From some experiments by Dr Irvine, it appears, that even in the more rapid action of the acids on metals, oxygen is absorbed from the air, either by the metal, or by the product of the decomposition of the acid acting in its nascent state, there being a small increase of weight, notwithstanding the escape of elastic products, during the solutions of silver and quicksilver in diluted nitric acid, and of zinc in diluted sulphuric acid *.

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* Essay on Chemical Subjects, p. 425.

The greater number of the metals burn in oxymuriatic acid gas, some of them, as antimony, arsenic, and, in general, the more volatile metals, with flame even at a common temperature; and all of them, except gold, silver, platina, and lead, when heated, exhibit the phenomena of combustion. The theory of this action is different, according to the view that is adopted of the constitution of oxymuriatic gas. According to the doctrine in which it is considered as a simple substance, it merely combines with the metal. In conformity to the common opinion, the oxygen of the oxymuriatic acid combines with the metal, and the oxide thus formed unites with the muriatic acid; and according to the opinion I have illustrated, the metal probably combines with the radical of the acid and with its oxygen, forming a ternary compound. The products of these actions, therefore, according to either of these latter views, are analogous to those formed by the action of the other acids on metals; that is, they are dry muriates: and in their properties they are perfectly analogous to other metallic salts. In the other they are chlorides, and, according to Sir H. Davy's view of the relations of chlorine, are more analogous to metallic oxides than to salts. The nomenclature he applies to them has been already noticed, and the probability of these views sufficiently considered.

When a metal has been oxidated, it becomes capable of combining with the acids, and exerts to them affinities of considerable force. No metal in its pure state unites with an acid; it must always be previously oxidated. If an acid, therefore, act on a metal, it first oxidates it directly or indirectly, in the modes which have been explained; and it combines with the oxide as it is formed: hence all solutions of metals in acids are, properly speaking, solutions of metallic oxides: and similar combinations are therefore formed, if the metal previously oxidated is added to the acid. If the compound of oxide and acid is insoluble, or of sparing solubility, it is precipitated as the action proceeds; if it is soluble, it remains dissolved in the water of the acid, and generally retaining an excess of acid.

The combinations of the metallic oxides with the acids are of a saline nature, similar in their general properties to the compounds formed by the acids with the alkalis or earths, the acid properties, when the due proportions are established, being neutralized, and the compound being often soluble in water, and crystallizable. From this strict analogy, these compounds have always been regarded as salts. Their nomenclature is similar to that of the other compound salts. They are named, according to the acid which enters into their composition, *sulphates*, *nitrates*, *muriates*, as sulphate of iron, nitrate of copper, muriate of quicksilver, &c. As the oxide of the metal, rather than the metal itself, is the base with which the acid is combined, they ought in strictness to be named sulphate of oxide of iron, or sulphated oxide of iron, &c.; but the other nomenclature is preferred, from being more concise, and more analogous to that of the other compound salts.

As the metals can combine with different proportions of oxygen, they may exist in different states of oxidation, in combination with the same acid, giving rise therefore to different compounds. On this subject a certain degree of generalization exists, presenting some important facts.

1*st*, If a metal be acted on by a diluted acid, or one of little energy of action, the combination formed is generally that of the metal in an imperfect or low state of oxidizement; while, by a more powerful or concentrated acid, the metal is more highly oxidated. Or, if the action be favoured by heat, the acid is more completely decomposed, and the metal receives more oxygen than when the solution proceeds at a low temperature.

2*dly*, After a metal has been dissolved in an acid, it may continue to attract oxygen, either from a farther decomposition of the acid, especially if heat be applied, or from the atmospheric air; and hence the changes which a metallic solution sometimes spontaneously suffers. This is the case principally with those metals which have a strong attraction to oxygen, as iron or tin; while the solutions of those which have a weaker attraction, remain permanent.

Lastly, The affinity of the acid to the oxide is varied by the degree of oxidation, being less powerful as the degree of oxidation is greater. A metal, therefore, saturated with oxygen, will frequently not remain in union with an acid, or at least will exert a weak attraction to it, while, if less highly oxidated, it forms a permanent combination. From this are explained the changes many metallic solutions undergo from exposure to the air. The metal in solution continues to attract oxygen, and its action on the acid becoming progressively weaker, it at length can retain only a small portion in combination, and an insoluble precipitate falls down, as is well illustrated in the example of a solution of sulphate of iron exposed to the atmosphere, in which, although the acid has by its action a tendency to maintain the metal in the state in which it exerts the most powerful attraction to it,—that in which it is least oxidated; yet such is the attraction of the iron to oxygen, that it absorbs it from the atmosphere, and approaches to the higher degrees of oxidation; and as it does so, the affinity of the acid to it diminishes; and at length a portion of the oxide, with a small quantity of the acid combined with it, precipitates, while the excess of acid remains in the liquor, with a small portion of the metal less oxidated, and which the acid, by its quantity adding to the force of its affinity, preserves in that state. Similar changes are produced by exposing a metallic solution to heat; a portion of the acid suffering decomposition, and the metal acquiring more oxygen. And from the same cause it sometimes happens, that an acid, in acting on a metallic oxide, causes by its action the expulsion of part of the oxygen, and then combines with the oxide thus partially reduced. On this principle, too, is to be explained the fact, that some metallic oxides are insoluble in sulphuric, nitric, or oxymuriatic acid, while they are dissolved by the sulphurous, nitrous, or muriatic acid; the latter acids abstracting a portion of oxygen from the oxide, and thus bringing it to that state in which its affinity to the acid can be exerted. Another important fact may be referred to it, established by the experiments of Gay Lussac, that a metallic oxide may precipitate either a different oxide of the same metal, or an oxide of another metal; the metal less highly oxidated precipitating the one in the higher state of oxidation. An extensive series of decompositions can thus be effected, some of which admit of useful applications *.

When a metal at different degrees of oxidation combines with an acid, are these degrees determinate or indefinite? This is an important question, not only theoretically, but likewise from its relations to pharmacy and some of the arts.

The opinion, that the metals enter into combination with the acids, in determinate degrees of oxidizement, was maintained by Proust †, and afterwards by Thenard ‡. There can be no doubt that this law is often observed, and that hence a number of metallic salts are uniform in composition. Quicksilver combines in two states of oxidation with muriatic acid; nor, whatever process may be followed, does it appear to combine with it in any intermediate degree. Some facts have been stated by Berthollet, in proof of the opinion, that the acids may unite with the metals in indefinite degrees of oxidation. Thus, in the case of a metallic solution which absorbs oxygen from the air, the absorption is gradual, from the *minimum* to the

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* Nicholson's Journal, vol. viii. p. 270.

† Nicholson's Journal, 4to, vol. i. p. 453. Journal de Physique, tom. lix. p. 334.

‡ Philosophical Magazine, vol. xxiv. p. 224.

maximum of oxidation; yet in no stage of the process is the combination of the oxide with the acid interrupted. The salts of iron, it has been supposed, consist of the metal in determinate degrees of oxidation; one, the green sulphate, at the *minimum;* the other, the red sulphate, at the *maximum.* Berthollet found, that on mixing solutions of these salts, an intermediate compound is formed, which the acid was unable to retain in solution. He also remarked, that in the crystallization of sulphate of iron, the crystals which are at first nearly without colour, become of a deeper colour in the subsequent crystallizations, until a liquor remains not capable of crystallizing, in which the metal is in the state of highest oxidation; proving that a division of the oxygen is made during the course of the crystallization, and that the sulphate of iron which crystallizes has not fixed proportions of oxygen. He has given a number of other observations in proof of the conclusion, that in many of these saline combinations, determinate degrees of oxidation are not observed *. They at least prove, perhaps, that the degrees of oxidation in which a metal combines with an acid, are more numerous than have been supposed.

The properties of the salts formed from the same metal, in different states of oxidation, united with the same acid, are extremely different. Quicksilver, in a low state of oxidation, forms with muriatic acid a compound insipid, and insoluble in water; while in a higher state of oxidation it forms with the same acid a compound acrid and soluble. Iron, in one state of oxidation, forms with sulphuric acid a crystallizable salt of a green colour; in another, a salt uncrystallizable, and of a reddish brown colour: and similar differences are found in the other metals.

The modern nomenclature is deficient in what relates to the salts of the same metal, in the different degrees of

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* Researches, p. 187. Chemical Statics, vol. ii. p. 346.

oxidation with the same acid; for as the name of the genus is taken from the acid, and that of the species not from the real base, which is the metallic oxide, but from the metal itself, it is difficult, by a variation of term, to denote the variation in the base. The distinctions have been usually derived from differences of properties, especially of colour, in which the salt of the same metal in different states of oxidation usually differ; hence the terms of green and red sulphate of iron, &c. Where the colour does not differ sufficiently, the distinction is drawn from other properties, as in the example of the mild, and the corrosive muriates of mercury. Dr Thomson's mode of distinguishing the oxides has been applied to the salts, as in the examples of proto-sulphate and per-sulphate, to denote the salts of the two oxides with sulphuric acid at the minimum and maximum of oxidation. Another method to convey the same distinction, is that of applying the usual generic term to the compound in the first degree of oxidation, and prefixing the epithet *oxy* to that at the maximum,—as sulphate, and oxy-sulphate. Both methods are liable to the objection already stated as applied to the oxides, that they lead into error, if the series of oxidation be not perfectly fixed. And the last is deficient, as it can be applied only to two compounds of each metal; and, as in the case of the muriatic salts, the term oxymuriate is employed in a different signification. They may be employed, however, to express the state of oxidation in the salt, though the specific appellations of particular compounds are perhaps best denoted in the usual mode.

Another important part of the history of metallic solutions, is that which relates to the proportions in which the oxides combine with the acids. The metallic oxides, like the alkalis and the earths, combine with the acids, in such proportions as to produce neutralization of properties. But the combination is not limited to these proportions: they also combine, so that there is an excess of acid, or an excess of base, forming compounds which have different qualities. When the base predominates, the compound approaches in its properties to the oxides; and such compounds have often been mistaken for oxides. When there is an excess of acid, it is difficult to obtain the compound in a crystallized, or even in a solid state. Rouelle pointed out the nature of these combinations *; and his views, though they were neglected, are more just than those afterwards entertained.

These diversities are best displayed in the decomposition to which the neutral combination may be subjected, either by the partial abstraction of its acid, or by the partial abstraction of its base. Thus the neutral sulphate of quicksilver may be obtained crystallized in slender prisms; but on submitting it to the agency of water, which exerts a stronger attraction to the sulphuric acid than to the oxide, it is decomposed; the greater part of the acid is attracted by the water, but it retains combined with it a portion of the oxide, while the greater part of the oxide is precipitated, holding an inferior portion of the acid in combination. The neutral sulphate is thus resolved into two salts,—a sub-sulphate, and a super-sulphate; and the existence of three compounds is thus demonstrated. The case is the same with a number of other metallic oxides and acids.

It is an object of inquiry, whether these combinations of a metallic oxide with an acid take place in determinate, or in indefinite proportions. Berthollet maintained the latter opinion †, that they are indefinite; or are rendered definite, only by the operation of cohesion and other external forces. And he considered this as established by the numerous stages of decomposition, through which a metallic salt may be made to pass by the agency of water,

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* Mémoires de l'Acad. des Sciences, 1754.

† Researches, p. 187. Chemical Statics, vol. ii. p. 542.

or of an alkali in different proportions, or by the application of heat in various degrees of intensity. The same conclusions are probably to be drawn with regard to these as to other saline compounds, though their definite composition has not been so fully demonstrated, nor the law regulating the proportions so clearly traced.

The important general principle announced by Gay Lussac with regard to the constitution of metallic salts*, that the quantity of acid in their composition, in the neutral state, is proportional to the quantity of oxygen in the oxide, which is their base, has been already pointed out. He inferred this law from the results of the decomposition of the salts of one metal by another metal. If into a metallic solution a different metal be immersed, the metal of the solution is often precipitated in its metallic form, while the other is dissolved in its place; it receives, therefore, the oxygen and the acid combined with the former metal. Thus zinc precipitates lead from its solutions in the metallic form, and a portion of zinc is dissolved: iron precipitates copper, and a portion of it is dissolved; and copper precipitates silver and quicksilver. Now, in all these cases, there is no evolution of acid; the precipitating receives the oxygen of the precipitated metal, and the oxide thus formed, neutralizes the quantity of acid which the oxide of the other metal neutralized. The quantities of these oxides may be different, that is, different portions of the different metals may have combined with the quantity of the oxygen present; but there exists such a relation between the oxygen and the acid, that the former remaining constant, the latter is proportional to it. It follows, therefore, that in all cases the quantity of acid in the metallic salt will be proportional to the quantity of oxygen in the oxide. Hence, if a metal combine with a large

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* Mémoires d'Arcueil, tom. ii. p. 159. Annales de Chimie, tom. lxxxv. p. 203.

quantity of oxygen, its oxide will require a large quantity of acid for its saturation; and of course, if the oxide require a large quantity of acid for its saturation, this indicates that the metal is combined with a large quantity of oxygen. The fact on which this law rests, that "a neutral metallic salt decomposed by another metal, changes its metal only," had been announced by Richter; and he concluded from it, that "the different metallic oxides which saturate a given portion of any acid, contain the same quantity of oxygen *." It affords, as has been already remarked, (vol. i. p. 155. vol. ii. p. 179.), a method of determining the constitution of all salts having an oxide for their base; for, if the proportion of oxygen in the oxide be found, that of the acid may be discovered; and it may equally be applied to determine the composition of the oxides, as, if the quantity of an acid which they saturate be found, the quantity of oxygen can be inferred, the quantity of an oxide which saturates the quantity of acid which another oxide does, containing the same quantity of oxygen.

The metallic salts are in general more susceptible of decomposition than the other orders of salts. With regard to many of them, the affinity of water to their acid is sufficient. The water, however, although it abstracts the acid, does not do so entirely, but the oxide retains a portion in combination with it, becoming, at the same time, generally insoluble; and, on the other hand, the acid, in combining with the water, retains a portion of oxide in combination, in consequence of its affinity towards it; and the proportions thus established in these combinations, are much influenced by the quantity of water to the action of which the salt is subjected.

Those metallic salts, which are not decomposed by water, may be decomposed by the alkalis, or by the more powerful of the earths. These decompositions present results somewhat complicated.

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* Nicholson's Journal, vol. xxx. p. 272.

The general action of an alkali on a metallic solution, is analogous to that of water, only more energetic. It causes its decomposition by abstracting the acid. But this abstraction, though it is usually to a greater extent than by water, is often partial; and the oxide precipitated retains a portion of the acid. These precipitates have been frequently regarded as pure oxides; but they seldom are so. That a portion of the acid remains in the combination, was shewn at an early period by Bayen, with regard to a number of them; and has been confirmed by the researches of other chemists. And according to the quantity of alkali which is used, the precipitate may vary in its composition. Thus, a little potash added to a solution of sulphate of copper, throws down a green precipitate; this Proust found to be an oxide of copper, with a portion of sulphuric acid, which the experiments of Berthollet *junior* have shewn to amount to seven parts in 100. If more potash be added, the precipitate acquires a blue colour; and in this state, according to the last chemist, it contains less acid. In some cases the whole of the acid appears to be abstracted, and these precipitates too, generally retain, as has been already remarked, portions of water.

The alkali, in decomposing metallic solutions, sometimes re-acts on the oxide, and dissolves a portion of it, forming a soluble ternary compound. Ammonia has more peculiarly this tendency: it has also been supposed, that it sometimes decomposes the oxide, its hydrogen attracting part of the oxygen, and reducing it nearly to the metallic state.

Metallic salts suffer decomposition from the different relations of the acids to their bases. The metallic nitrates are thus decomposed in the humid way, by muriatic, sulphuric, and phosphoric acids, which in general combine with the oxide; and other decompositions are produced, either by single or double attraction, by the application of heat. These results were formerly considered as arising from the different forces of affinity of the acids to the metallic oxides; muriatic acid being supposed to have the strongest attraction; next to it the sulphuric and phosphoric; while that of the nitric or carbonic was regarded as weaker. They are probably in a great measure owing to the force of cohesion; since the decomposition is only apparent where there is precipitation, and the superior affinity has always been ascribed to that acid which forms with the metallic oxide the least soluble compound.

The last kind of decomposition of the metallic salts, is that from the operation of another metal. It is peculiar in this respect, that the metallic oxide, in combination with the acid, is not separated, but is decomposed: its oxygen, as well as the acid combined with it, are abstracted: it is reduced, therefore, to the metallic form, while the metal effecting this decomposition is dissolved in its place. Thus a wire of copper, immersed in a solution of nitrate of silver, precipitates the silver; or a wire of iron, immersed in a solution of sulphate of copper, precipitates the copper; the precipitating taking the place of the precipitated metal: so that in the former of these cases, nitrate of copper, in the latter sulphate of iron, is formed.

In these decompositions different quantities of the metals are requisite to precipitate each other. This was observed by Bergman. In his dissertation on the quantities of phlogiston in metals, he observed, that if 100 parts of silver be dissolved in the requisite quantity of nitric acid, it will require to precipitate it, 234 parts of lead, which will be dissolved in its place, 174 of bismuth, 135 of quicksilver, 88 of tin, 64 of nickel, 31 of copper. From such experiments Lavoisier inferred, that the quantities of oxygen with which the metals combine might be ascertained; for, as the precipitation of the one metal by the other depends on the transfer of the oxygen, the same quantity of oxygen must have been combined with these different quantities of the different metals. Since 31 parts, for example, of copper, are sufficient to precipitate 100 of silver, it follows, that 31 parts of the former metal can take all the oxygen with which 100 of the latter combine: and of course, the quantity of oxygen combined with 100 of silver, when it is brought to the state of oxide, is equal to that combined with 31 of copper in the same state. Proceeding on this principle, he prosecuted these experiments *. It is not proved, perhaps, that each metal is brought to a similar degree of oxidation, as the affinity of the acid may interfere, and determine the combination at some particular proportion different from this.

These decompositions were ascribed by Lavoisier, or rather by Bergman, (for the speculations of the latter chemist required only a change of terms to adapt them to the modern theory), to the relative forces of affinity of the different metals to oxygen; those which had a stronger attraction to it precipitating those which had a weaker, the acid being considered merely as the medium, which, by the fluidity or solubility which it communicated, allowed these affinities to operate. And from the series of these decompositions, the order of affinities of the metals to oxygen was inferred †.

They may in part be owing to this cause; but other causes likewise operate. A proof of this is, that if we take three metals, of which the second shall decompose the solution of the third, and precipitate it in its metallic form, and the first decompose, in like manner, the solution of the second; this first metal, which decomposes the solution of the second, will not decompose, or will decompose only partially, the solution of the third. Thus, copper decomposes a solution of quicksilver, and iron decomposes a solution of copper, but iron does not decompose, or decomposes very imperfectly, a solution of quicksilver. This

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* Mémoires de l'Acad. des Sciences, 1782, p. 512.

† Ibid. 1782, p. 512.

proves, that something more than the relative affinities of the metals to oxygen, is the cause of these decompositions.

One modifying circumstance is the affinity of the precipitating to the precipitated metal. Thus the copper, in this example, precipitates the quicksilver from its solution more readily than the iron does, though the latter has probably a stronger attraction than the copper to oxygen, because, between the copper and quicksilver there exists a mutual attraction, while there is scarcely any between quicksilver and iron. Hence also, the metal which is precipitated is seldom perfectly pure, but has a portion of the precipitating metal combined with it *. It is probable, too, that the different affinities of the acid to the different oxides may influence the results.

There is also reason to believe, that galvanic action has a share in these decompositions, or at least in the production of a phenomenon which often accompanies them,—the deposition of the precipitated metal in a symmetrical or crystallized form. If zinc be suspended in a solution of acetate, or nitrate of lead, the lead is precipitated on the surface of the zinc, and it extends from this in filaments, or in broad leaves or plates, until the whole lead is deposited. Silver precipitated from its nitrous solution by quicksilver, takes a still more regular form, rising from the globule of quicksilver immersed in the solution in a group of prisms. This has been named Metallic Arborescence. It was observed, in the case of lead precipitated by zinc, that the ramifications increase, not from the surface of the zinc, but from the extremities of the ramifications already formed of the lead; and this could not therefore be ascribed to any chemical action of the zinc, but to the action of some power at the part where the new deposition takes place. Sylvester supposed it to arise from the operation of galvanism. The commencement of

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* Berthollet, Researches on Chemical Affinity, p. 125.

the action is chemical; the zinc reduces the metal of the solution by its superior attraction to oxygen; but from the layer of reduced metal, deposited on its surface, a galvanic arrangement is formed, and the remainder of the process is galvanic. The water of the solution is probably decomposed; its oxygen is retained at the positive surface, that of the zinc, and combining with the metal, forms oxide of zinc, which is dissolved by the acid present; and its hydrogen being attracted, according to the established law, to the negative surface, which is the extremity of the reduced metal, operates in the farther reduction of the dissolved metal, attracting the oxygen combined with it; it is deposited at that extremity, and hence the accretion proceeds from that point *. Grotthus gave a similar view; and he farther established rather a singular fact, that a new metal might be attached to the extremities of the ramifications of the metal first precipitated. Thus, if a solution of nitrate of copper be placed beneath a solution of nitrate of silver in the same vessel, if the silver be precipitated by the immersion of a copper wire in its solution, the filaments, extending downwards, will at length pass into the solution of copper; and when this happens, reduced copper will be attached to the extremities of the ramifications of silver; a proof, as Grotthus justly remarked, 1*st*, That the arborization of metals precipitated from their solvents, is formed by superposition of their particles on one another; and, 2*dly*, That since neither copper nor silver has of itself the power of reviving the metal contained in nitrate of copper, those two metals were rendered capable of producing this effect only in virtue of a current of galvanic electricity, resulting from their mutual contact †.

In some cases the decomposition of a metallic salt by

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[*] Nicholson's Journal, vol. xiv. p. 96.

[†] Ibid. vol. xxviii. p. 121.

another metal is partial, a part only of the oxygen being abstracted; and the two metallic oxides which are formed are precipitated in combination.

Inflammable substances, as might be expected from their affinity to oxygen, are capable of effecting similar decompositions of the metallic solutions. An extensive series of experiments on this subject was performed by Mrs Fulhame *, from which it was established, that such decompositions were effected by the agency of phosphorus, sulphur, charcoal, hydrogen, sulphuretted hydrogen, and phosphuretted hydrogen gases. The manner in which they were executed, was to immerse a piece of silk in the metallic solution, and, while humid, expose it to the action of the phosphorus dissolved in ether, the charcoal dissolved by an alkali, the sulphur in vapour, or the other substances in their elastic state: a change of colour is induced, and the metal soon appears with all its lustre. A singular fact was established by these experiments, not yet satisfactorily accounted for, that the presence of water is indispensable to the complete reduction of the metal.

Some of these substances precipitate the metals by being immersed in the metallic solution. This is the case with phosphorus and charcoal. In the reduction by phosphorus, the same cause appears to operate as in the reduction of one metal by another,—the affinity exerted to the metal which is precipitated; those metals which have a strong attraction to it, being more readily precipitated than those that have a weak attraction, even though the latter may have at the same time a weak affinity to oxygen: thus gold is less speedily and abundantly precipitated than copper †. The phosphorus, too, from the experiments of Schnaubert, appears to combine with some of the metals

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* Essay on Combustion.

† Researches on Chemical Affinity, p. 125.

which it thus precipitates, as with silver, quicksilver, and tin *. Similar metallic phosphurets, according to Grotthus, are obtained by adding a solution of phosphorus in alkohol, to the solutions of gold, silver, quicksilver, and copper. The other metals are not reduced by it in this form, but their oxides are precipitated; and if a little alkali has been dissolved in the phosphuretted alkohol, combinations of the metallic oxide with the phosphorus are formed.

Light decomposes a number of metallic solutions, either partially de-oxidating the metal, or reducing some of them to the metallic state. According to Mrs Fulhame's observations, it requires the presence of water to produce the effect.

The alkalis, in decomposing the metallic salts, sometimes combine with the oxide and the acid, forming a ternary compound. They are also capable of dissolving a number of the metallic oxides, independent of the presence of any acid. Thus the oxides of tin and lead are dissolved by a solution of potash or soda; those of copper, zinc, and cobalt, by ammonia. In the dry way, and at an elevated temperature, the fixed alkalis are also capable of combining with a number of the oxides, and of forming vitrified compounds. It appears even, that the action of an alkali may be so energetic, as to aid the oxidation of a metal. Thus tin is oxidated at a natural temperature by atmospheric air, when it is acted on at the same time by a solution of potash.

The acids, it has been stated, exert stronger affinities towards metals in a low, than in a high state of oxidation; and hence they favour the disengagement of the oxygen from the more perfect oxides. The alkalis observe the opposite law, or have a stronger tendency to combine with the metals in a highly oxidated state. Hence they resist

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* Nicholson's Journal, vol. viii. p. 158.

the disengagement of oxygen by heat. This difference is well illustrated in the comparative result of exposing to heat black oxide of manganese with sulphuric acid, or with potash; in the first case, much of the oxygen is expelled; in the second, none is expelled, though the heat is more intense.

According to the observations of Klaproth, the solutions of the metallic oxides in the alkalis are decomposed, and the metal is precipitated, in its metallic state, by the action of another metal, which is soluble in the alkali, and which exerts a stronger attraction to the oxygen, in the same manner as the solutions of metals in acids are decomposed. He thus precipitated tungsten, from the solution of its oxide in ammonia, by zinc *.

The metals, either in their metallic or oxidated state, do not form any combination with nitrogen. Hydrogen exerts towards some of them a weak affinity; it combines in particular with arsenic, forming a permanent gas; there is also reason to believe that they form a solid compound: it displays similar relations to tellurium, and to potassium. Some other metals have been supposed to be dissolved in small quantity by hydrogen gas, but this is doubtful.

Carbon combines with few of the metals, probably from its infusibility. In reducing some of the metallic oxides, however, as those of iron, by carbonaceous matter, at a high temperature, the metal, in passing to the metallic form, unites with a portion of the carbon; and a larger quantity can be combined with it, by exposing thin bars of the metal, imbedded in charcoal powder, to a strong heat. By a process of this kind, steel, which is a carburet of iron, is formed.

With sulphur a number of metals, all of them indeed, except gold and zinc, form combinations by fusion; and a

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* Nicholson's Journal, vol. xiii. p. 187.

number of metallic sulphurets exist in nature. They retain some of the metallic properties, particularly lustre and opacity, and a considerable specific gravity. They are destitute of ductility or malleability, and are generally more fusible than the metal of which they consist.

A striking phenomenon, already taken notice of, occurs in these combinations of sulphur with the metals. When the temperature is raised sufficiently high to melt the sulphur, and the combination commences, heat is evolved, and a glow of light, similar to that of ignition, is produced. This appearance was observed by Scheele [*], and afterwards made the subject of experiment by the Associated Dutch Chemists [†]. They exposed to the heat of a charcoal fire, in a close phial, a mixture of sulphur with copper, iron, zinc, and tin, in the proportion of nearly three parts of any of the metals to one of sulphur; this proportion being found, from various trials, to succeed best; and found, that in all of them the luminous appearance took place, soon after the sulphur had passed into a state of fusion. That from copper and sulphur, or iron and sulphur, was extremely bright: it was not exhibited by antimony, bismuth, or cobalt. The experiment succeeded *in vacuo*, or under hydrogen gas, or carbonic acid gas, and even under quicksilver; and likewise when the materials were previously thoroughly dried. The residual matter appeared to be the sulphuret of the metal, without any indication of having received oxygen. Trommsdorff ascertained, that the experiment performed with the metallic oxides instead of the metals, was attended with no production of heat or light [‡].

It was supposed, that the phenomena exhibited in these combinations, afforded an objection against the antiphlo-

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[*] Treatise on Air and Fire, p. 155.

[†] Journal des Mines, No. II. p. 85.

[‡] Journal de Physique, 1794, p. 178.

gistic theory, the phenomena of combustion being produced without the combination of oxygen; and to obviate this, some chemists supposed, that the sulphur either contained oxygen, or contained water, from which oxygen might be derived. But this supposition does not appear to be well founded, and there is no necessity to recur to it; it is obvious, that the extrication of heat and light may attend other chemical combinations as well as those of oxygen; and that this is no objection to the doctrine, that the usual cases of what is considered as combustion,—the burning of sulphur, of phosphorus, &c. are combinations of oxygen with these inflammables.

It has been supposed, that the combinations of sulphur with the metals take place in one or two determinate proportions, and this opinion has in particular been maintained by Proust *. He was under the necessity of admitting, indeed, that an additional quantity of sulphur may be combined with the metallic sulphuret, which is perhaps only a different mode of representing the fact, that the proportions are less limited. And the native sulphurets are very variable in their proportions, as Vauquelin and Klaproth have shewn †. But these variations may be owing, in part at least, to intermixture. The general law of chemical combination leads to the conclusion, that the proportions of sulphur and metal must be definite, and in a number of these sulphurets they appear to be so. It has also been shewn, particularly by Laugier ‡, that even when they are prepared from different proportions of the materials, the real combination is established in a uniform proportion, and that if an excess of sulphur be present it is easily volatilized. The greater number of the metals seem to combine with only one definite proportion of sulphur. Some,

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* Journal de Physique, tom. lix. p. 260. lxxxi. p. 255.

† Ibid. tom. lv. p. 349.

‡ Annales de Chimie, tom. lxxxv. p. 58.

however, unite with two proportions, particularly quicksilver, iron, tin, lead, nickel, and arsenic. These compounds are distinguished by the terms of sulphuret and super-sulphuret. So far as has been investigated, the law of definite proportions is observed, the higher proportion of sulphur being a simple multiple of the lower. In magnetic pyrites, for example, 100 of iron are combined with 58.5 of sulphur, and in common pyrites with 117. Berzelius has stated the general law with regard to the sulphurets, that the proportion of sulphur to the metal is such, that when oxygen is communicated to the compound, so as to oxidate the metal, and convert the sulphur into sulphuric acid, a neutral compound is formed; the same quantity therefore of sulphur, that exists in a metallic sulphate, exists in a sulphuret of the same metal. And also, what is a consequence of the combining weights of these elements, that the sulphur, in the first proportion in a metallic sulphuret, is twice the weight of the oxygen in the prot-oxide of the same metal, the quantity of metal being the same.

The combination of the sulphur with the metals is so intimate, that it is expelled only partially by a high temperature; and if the heat be intense, the sulphuret itself is sublimed. If the air be admitted, the sulphur is more completely abstracted, by being converted into sulphurous acid; and by this operation the native sulphurets are decomposed on a large scale, to obtain their metals. The circumstances of this have been pointed out particularly by Descostils, with a view to the proper metallurgic treatment of the sulphuretted metallic ores *.

By combination with sulphur, those metals which have a strong attraction to oxygen, as iron, become more susceptible of oxidation. Hence such sulphurets, exposed to air and humidity, attract oxygen, and pass to the state of

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* Mémoires d'Arcueil, tom. ii. p. 424.

sulphate: those which have a weak attraction to oxygen, or a strong attraction to sulphur, do not suffer this change: and a metal in the state of super-sulphuret is also less liable to it. Muriatic acid, or sulphuric acid somewhat diluted, enables the metal of a metallic sulphuret to decompose the water present, and sulphuretted hydrogen is disengaged. Sulphuric acid, in its concentrated state, and with the assistance of heat, in acting on these sulphurets, suffers decomposition, its oxygen, as Berthollet observed, being shared between its sulphur and the sulphur combined with the metal, so that it is converted into sulphurous acid. Nitric acid oxidates the metal, and if previously diluted, separates the sulphur; if concentrated, part of the sulphur is also oxidated. The metallic super-sulphurets are less liable to these changes from acids than the sulphurets.

Sulphur combines with the metallic oxides: these compounds may be named sulphuretted metallic oxides. They exist in nature, and may also be formed artificially by a moderate heat: if the heat be increased, they are decomposed, the sulphur attracting the greater part, or the whole of the oxygen, and forming sulphurous acid, while a portion of it often remains combined with the metal. According to Vauquelin, sulphur has a stronger attraction to the metals than to their oxides, and its affinity to the oxides becomes weaker as they are more highly oxidated*. Acids dissolve the oxide, and precipitate the sulphur.

Sulphuretted hydrogen acts on the metals and their oxides. It quickly tarnishes the surface of the metals, and if they are long exposed to it, scales of metallic sulphuret are formed. It combines with the oxides, and sometimes is decomposed by them, reducing them to the minimum of oxidation, or to the metallic state. If its watery solution be added to the solution of a metallic salt, a precipitate is generally formed. This precipitate is sometimes the result

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* Nicholson's Journal, 4to, vol. v. p. 318.

of the immediate combination of the sulphuretted hydrogen with the oxide; but in many cases a decomposition takes place; the hydrogen of the sulphuretted hydrogen attracting partially, or completely, the oxygen of the metallic oxide, while the sulphur combines with the metal, forming a sulphuret, or with the oxide of the metal at the *minimum* of oxidation. Those metals, to the oxides of which, in this state of *minimum*, sulphur has no great affinity, are not precipitated from their solutions in acids by the solution of sulphuretted hydrogen, but remain in combination with the acid. Such are iron, manganese, cobalt, and nickel. But when an alkali is present to saturate the acid, they are thrown down, and accordingly, they and the other metals are precipitated by the hydro-sulphurets, and sulphuretted hydro-sulphurets, from actions of this kind being exerted. According to Gay Lussac, the metallic oxides in which oxygen is greatly condensed, such as those of iron and zinc, do not decompose the hydro-sulphurets; all the others do, and form water, sulphites or sulphuretted sulphites, and frequently metallic sulphurets *.

Gay Lussac has also advanced, with regard to these precipitations, the principle,—that the quantity of sulphuretted hydrogen expended, is proportional to the degree of oxidation of the metal, and this whether its hydrogen combines with the oxygen of the oxide, so as to reduce it to the state of metal with which the sulphur unites, or whether the sulphuretted hydrogen combines with the oxide, without either being decomposed †.

The action of sulphuretted hydrogen on the metallic oxides affords the most delicate test of the presence of a metal, as it forms, with their solutions in acids, precipitates usually of dark colours. It is sometimes applied in the form of its watery solution; but as there are some which

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* Nicholson's Journal, vol. xxxi. p. 74.

† Memoires d'Arcueil, tom. ii. p. 175.

are not precipitated in this mode, it is more usually employed under the form of an alkaline hydro-sulphuret, the base of which saturates the acid of the metallic salt, and allows the sulphuretted hydrogen to act on the oxide. The precipitates thrown down from the different metals, are frequently of peculiar shades of colour, which serve to distinguish them, though these are liable to variation from the state of the combination, and particularly the degree of oxidation. The alkaline sulphuretted hydro-sulphurets, or the hydroguretted sulphurets, as they are named, likewise decompose the metallic salts, the alkali neutralizing the acid, and the super-sulphuretted hydrogen combining with the oxide; the precipitates thus formed contain an excess of sulphur.

The alkaline sulphurets act on the metals. If sulphuret of potash be exposed to heat with a metal in filings, a combination is established; even gold, which cannot be directly combined with sulphur, can thus be combined with it, as Stahl observed. The reason of this appears to be, as Berthollet has remarked, that in attempting to combine gold and sulphur by heat, the affinity not being strong, the cohesion of the gold resists it, and the heat cannot be raised sufficiently high to diminish this, without volatilizing the sulphur; but when the sulphur is combined with a fixed alkali, its volatility is restrained, and the temperature may be raised so as to combine it with the gold. There is a singular fact with regard to this combination, that it is soluble in water, the alkali being supposed to hold the metallic sulphuret dissolved; and hence, when an acid is added to the solution, the metal and sulphur are precipitated in combination. It may be doubted, however, whether the theory of this operation is altogether understood; it is rather improbable that the alkali should have such energy of action; and the nature of the precipitate which an acid throws down has not been well ascertained.

Phosphorus forms combinations with the metals. From its volatility and combustibility, these are not easily effected by exposing it with the metal to heat. Margraaf, however, succeeded in obtaining in this way the phosphurets of arsenic, zinc, and copper. The process employed by Pelletier, who made a series of experiments on these combinations, succeeds better *. It consists in heating phosphoric acid and charcoal with the metal: the charcoal attracts the oxygen of the acid; and the phosphorus, as it is re-produced, combines with the metal. The metallic phosphurets have generally a degree of metallic lustre: they are frequently soft, especially if the phosphorus be in large proportion, and, if hard, are brittle: they are more fusible than the metals of which they are formed, and more combustible. They are partially decomposed by heat.

The metals combine with each other by fusion. The name of Alloy is given to these compounds. They retain the general metallic properties,—lustre, opacity, and density; and even in the greater number of cases, the properties of the constituent metals remain in the combination, only somewhat modified. The colour is often altered. In general the alloys, too, are more hard and brittle than the individual metals of which they consist; and frequently very considerably so; though these, as well as the other changes of properties, are influenced by the proportions †. They have also a greater fusibility than the mean fusibility of the respective metals. The metals in these combinations are more susceptible of oxidation than in their separate state, probably owing to the diminution in the power of cohesion by the combination.

Though the general metallic qualities, and often the specific qualities of the metals combined, remain in these compounds to a certain extent, yet these are also often much modified, or altogether disguised; and this is the

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* Mémoires de Chimie, tom. i. p. 212. and ii. p. 22.

† Chemical Statics, vol. ii. p. 501.

case, not only with the physical qualities, changes in which may be conceived to happen from the condensation and new arrangement of the particles to which the combination gives rise, but with the more essential chemical properties. The volatility, for example, of the more volatile metals is often restrained by their combination with those more fixed, so that after they have been united, they cannot be entirely separated by heat, as in the example of gold and arsenic. Even their relations to the most powerful reagents are changed. Thus in the operation of cupellation it is known, that gold protects copper, when present in a certain proportion, from oxidation. A striking example of this, too, is afforded in the alloy of antimony and tin. Thenard, examining an alloy of these metals, which was introduced into commerce, found that muriatic acid had hardly any effect upon it, though it dissolves tin readily, the antimony protecting the tin from its action: nitric acid merely oxidated it without dissolving any portion of it; and when the product of this action, consisting of the oxides of the two metals, was dissolved in muriatic acid, they were both precipitated by water, although the oxide of tin alone would not have been thrown down. Sulphuretted hydrogen too, which precipitates oxide of tin with much difficulty, precipitated it rapidly and copiously in combination with the antimonial oxide*. These facts shew the important effects which arise from the mutual affinities of the metals, both in their metallic and oxidated state.

A degree of condensation usually attends the combination of the metals, so that the specific gravity of the compound is greater than the mean specific gravity of its constituents: in brass, which is an alloy of zinc and copper, it is one tenth greater; and in some cases, the condensation is such, that the density is even greater than that of the heavier of the metals combined, as in the alloy of silver

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* Philosophical Magazine, vol. xxiv. p. 256.

and quicksilver. Sometimes, however, the particles assume such an arrangement, that the density is less than the mean, as in the examples of the alloy of copper with silver, of gold with tin, and gold with iron.

In these combinations, a difference is observed in the attractions exerted, so that one metal is more disposed to unite with another than a third: it is not however considerable: hence three, four, or more metals, can be combined together. Some refuse to unite, as iron and lead, and iron and quicksilver. The combination is in part regulated by the relation of fusibility and specific gravity; so that the affinities being equal, the metals are less disposed to combine, as they differ more in fusibility and specific gravity; and where the affinity is weak, a considerable difference of this kind may prevent combination. The same cause appears often to place limits to the combination, or to regulate the proportions in which it takes place. The influence of the specific gravity in this respect, is established by a fact, known to the older chemists, and observed by Bergman, in the alloy of iron and tin, and by Guyton in the alloys of silver and lead, and silver and iron, that the upper and under parts of a metallic alloy formed by fusion, frequently differ in the proportions of the ingredients, the under portion containing more of the heavier metal, the upper more of the lighter. When a large quantity of one metal, however, is melted with a small quantity of another, the combination is generally uniform; the quantity adding so much to the force of affinity, as to overcome any counteracting property, while, if other proportions are observed, two separate alloys, with different proportions, one containing a large quantity of one metal, and the other a large quantity of the other, are obtained *. The proposition has been maintained both by Dalton and Berzelius, that definite proportions conform-

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* Researches on Chemical Affinity, p. 75.

able to the usual laws, are established in these combinations. Some facts confirm this, certain alloys, such as brass, the alloy of copper and zinc, being composed of the metals in one or two uniform proportions. But it is more difficult to establish the principle, from the influence of fusibility giving rise to an intermixture of one or other metal.

The art of soldering depends on the formation of an alloy; the solder being a metallic compound of greater fusibility than the metal or metals designed to be united, and serving also by its affinity to them to unite them. The arts of gilding, silvering, and tinning, depend also on the mutual affinity which the metals exert.

The metals exert no attractions to the earths. The metallic oxides, however, unite with several of the earths by fusion: they render them more fusible, and form glasses which have often brilliant colours.

The metals are found in nature in various states. When uncombined, or when combined only with each other, they are said to be native. When combined with other substances, so that the metallic properties are in some measure disguised, they are said to be mineralized, or in the state of Ore. The substance with which the metal is combined, is termed its Mineralizer. The most common states of combination in which the metallic ores are found, are oxides, combinations of oxides with the acids, particularly carbonic, sulphuric, muriatic, and phosphoric, and sulphurets. These are met with generally in veins penetrating rocks; and are usually blended or intermixed with various earthy fossils,as calcareous spar, fluor spar, quartz, &c. Some metallic ores occur in beds, or in large insulated masses.

To obtain the metal after it has been extracted from the mine, various operations are requisite. The ore must be separated from the accompanying earthy fossils, which is done as much as possible by the hammer. Where the ore and the earthy matter are more intimately mixed, advantage is taken of the difference in their specific gravity. The whole, after being coarsely pounded, is washed with water on an inclined plane; the water carries forward the earthy substances, and the heavier metallic matter remains behind. After this operation, the ore, if it contain sulphur or arsenic, or any acid, is subjected to a low red heat, which is termed roasting it, and by which any of these substances is expelled. It is lastly necessary to reduce it to the metallic state. This is done by placing in a furnace alternate layers of coaked coal, or charcoal, and the metallic matter: a strong heat is excited by a blast of air: the carbonaceous matter attracts the oxygen; and the metal is reduced, melted, and run out at the bottom of the furnace. The volatile metals are obtained by sublimation or distillation. Even after these operations, the metal is seldom pure, but is combined with other metals, which have been present in the ore. If these are in small quantity, and have no injurious effect, they are in general disregarded. If it is necessary to separate them, or if, from their value, this becomes an object of importance, different processes are followed, adapted to each, which will require to be noticed under the different metals.

The art of assaying metallic ores, is that of analysing them in small quantities, so as to discover their component parts. The general process consists in selecting proper specimens of the ore, which is done by taking equal portions of that which appears to be the richest, the poorest, and of medium value, and reducing these to coarse powder; this is washed, to carry off any earthy or stoney matter: it is then roasted in a shallow earthen vessel under a muffle, to expel the volatile ingredients: it is lastly reduced by mixing it with three times its weight of black flux, and exposing it to the requisite heat; using other fluxes, and applying a more or less intense heat, as the metal is more or less refractory. The metallic matter existing in the ore is thus obtained. This, it is obvious, may consist of various metals; and if there is reason to believe this, it is submitted to operations generally conducted in the humid way, and adapted to the metals which may be supposed present. Sometimes also, an accurate analysis is made at once of the metallic ore in the humid way; the metal being dissolved by the different acids, and precipitated by the alkalis, earths, prussiate of potash, by sulphuretted hydrogen, and other re-agents. The more minute details of the process will be given in describing the modes of analysis, by which the composition of mineral substances is determined.

Besides being found in the earth, several of the metals are constituent principles of organized matter. Iron is contained in the blood, and in some other animal products, and it, as well as gold and manganese, can be abstracted from the ashes of plants.

The class of metals has been subdivided into orders, under which the individual metals are arranged. Gold, silver, and platina, preserving their lustre on exposure to the air, possessing a high degree of ductility and malleability, and not being oxidated when exposed to a high heat, have been placed in one order, under the appellation of Perfect or Noble Metals. Quicksilver, copper, iron, tin, and lead, possessing ductility and malleability, but being oxidated by heat, have been placed together under the name of Imperfect Metals. The others, zinc, antimony, bismuth, cobalt, nickel, manganese, arsenic, (and the greater number of the newly discovered metals may be added to this order), having little ductility or malleability, were termed Semi-Metals. This was the old division: others have also been introduced; but any classification of this kind is inaccurate; no advantage is gained by forming such orders, and they are altogether artificial: each metal forms a species, and they may be considered individually in that order in which the transition is most natural, beginning with those which have the characteristic metallic properties, tenacity and specific gravity, in the highest degree. Those of recent discovery, and which are only imperfectly investigated, may be placed after the others.

There is reason to suspect, that among the bodies arranged as metals, there are some which are alloys. This suspicion applies more particularly to those which are found in sparing quantity in nature, and which are not distinguishable by very characteristic properties, but rather by minute differences. The properties of metals are disguised in many cases by their combination with each other; and there are several alloys, the component parts of which it is scarcely possible to separate, so that if we had not actually formed them, we should not have been able to discover their composition by analysis, but have been led to regard them as simple metals. This strengthens the probability, that some of those substances, placed as distinct metals, may be undiscovered alloys. This conjecture will apply principally to those which are found as it were insulated, existing perhaps merely in a particular fossil, and which have no very distinctive character, nor any very marked chemical action. It is a just observation by Mr Chenevix, that metallic alloys are in general brittle compared with the metals of which they are formed; and it is therefore among the brittle metals, or what have been named the Semi-metals, that we may expect the simplification of the class.

CHAP. I.

GOLD.

Gold holds the first rank among the metals, from its great ductility, malleability, specific gravity, and the richness and permanence of its colour and lustre. Platina is somewhat superior in specific gravity; but is inferior in some of the other characteristic metallic qualities; and as platina is more allied in its general qualities with silver, it may follow or precede that metal, and the first place be allowed to gold.

Gold is found native, either pure or alloyed, with other metals, particularly with silver, and tellurium. It is sometimes contained in other metallic ores, particularly in some varieties of pyrites, in which it is supposed to be mechanically disseminated. It appears to exist in the vegetable kingdom; the experiments of Rouelle, Sage, and others, having shewn, that it can be extracted in small quantity from the ashes of plants.

The extraction of native gold from the foreign matter with which it is mixed, is performed by amalgamation with quicksilver. After having been freed, by pounding and washing, from the earthy matter, it is triturated with quicksilver: the amalgam is subjected to pressure in leather, by which the more fluid part is separated, while the more consistent amalgam, containing the greater part of the gold, remains. From this the quicksilver is distilled in retorts of earthen ware, and the remaining gold is afterwards fused. When gold is contained in other ores, the ore is roasted to expel the more volatile principles, and to oxidate the other metals: the gold is extracted by amalgamation, by liquefaction with lead, by the action of nitric acid, or other methods adapted to each ore according to its constituent parts.

Gold obtained in any of these ways, is usually alloyed, particularly with silver and copper. The first step in its purification is the process of Cupellation. To explain this, it is necessary to observe, that gold, silver, and platina, are incapable of oxidation by atmospheric air, aided by heat; but any other metal undergoes this change. If any metal, therefore, with the exception of silver and platina, be combined with gold, it may be abstracted by its oxidation, the alloy being melted and exposed to the action of the air. If the foreign metal, however, be not very susceptible of oxidation, as copper, a portion of it is protected from oxidation by the affinity the gold exerts to it, and the oxide of this and some other metals is also very difficult of fusion and vitrification. These obstacles are removed by the addition of lead, this metal being very fusible, extremely easy of oxidation, forming an oxide which easily vitrifies, and which favours the oxidation and vitrification of other metals. A portion of it, therefore, is added to the impure gold, more or less according to the quantity of alloy it contains. They are melted and exposed to heat on a cupel, (which is a vessel made of bone ashes, or sometimes of wood ashes), under a muffle placed in a furnace, or, in the large way, on the hearth of the refining furnace. The lead passes to the state of oxide, and promotes the oxidation of the foreign metals, and, combining with the other oxides, renders them more susceptible of fusion or vitrification. The vitrified oxide is absorbed by the porous cupel, or, in the large way, the greater part is driven off by the blast of bellows. As the fused gold becomes pure, it exhibits various prismatic colours, which succeed each other quickly: it at length suddenly brightens, or its surface becomes highly luminous. This is regarded as the completion of the process: the metal is allowed to become solid, and while yet hot is detached. The whole operation requires much practical skill, particularly with regard to regulating the heat properly in the different stages.

The gold, after this process, may still be alloyed with silver, which, being nearly as difficult of oxidation, is not removed by the action of the lead. It is therefore subjected to the operation of Parting. The metal is rolled thin, and cut into small pieces: these are digested in diluted nitric acid, which dissolves the silver, leaving the gold undissolved in a porous mass. It has been found, however, that when the proportion of silver is small to that of gold, the latter protects the former from the action of the acid: the previous step of Quartation, as it is named, is therefore employed, consisting in fusing three parts of silver with one of gold, thus reducing the gold to one fourth of the mass, and subjecting this alloyed metal to the operation of the acid. These operations form what is named the Assay of Gold, which is practised not only with the view of obtaining gold pure, but of determining the purity of the gold of commerce, or the proportion of foreign metals with which it is alloyed, a given portion of the mass being submitted to experiment.

There is a peculiar language in commerce, often referred to by chemical authors, to denote the purity of gold, or the degree of its alloy with other metals. The mass is supposed to consist of 24 equal parts, which are named Carats. If perfectly pure, it is said to be gold 24 carats fine: if alloyed with one part of any other metal, or mixture of metals, it is said to be 23 carats fine. The degree of purity can be judged of with considerable accuracy by those experienced in the art of assaying, by the colour and lustre of the fresh fracture, and the hardness and tenacity. The method by the streak, allows of a still more correct estimate. A line or streak is drawn, by impressing the metal on a close grained dark-coloured stone, generally basalt, hence named the Touch-stone; the streak is compared, in colour and lustre, with the streak impressed in a similar manner by needles of alloys of the more common proportions, the composition of which is exactly known, and the one to which the metal subjected to trial approaches most nearly, is thus discovered. Sometimes this method is aided, by allowing a drop of diluted nitric acid to fall on the streak, and observing if it cause any change in its lustre, and to what extent.

Gold, perfectly pure, is of a rich yellow colour, inclining to red: its lustre is not impaired by exposure to air or moisture; its specific gravity is 19.25, and when hammered 19.36, inferior only to that of platina. In malleability it is superior to all the metals: in the finest gold-leaf, it is calculated by Magellan, from the weight of a known number of the leaves of a measured surface, that one grain of gold is extended to above 56 square inches. It suffers even a greater extension than this in the gilding of silver wire. Its ductility is also very great, so that it can be drawn into very fine wire. Dr Wollaston has shewn, that by inclosing a wire of gold in a hollow cylinder of silver, and extending the cylinder, the gold will be extended so far, that a wire of it, 500 feet in length, weighs only 1 grain. In hardness, it is inferior to iron, platina, copper, and silver.

Gold melts at 32° of Wedgwood's scale. When in fusion, its colour is a brilliant sea-green. It crystallizes by slow cooling in minute octaedrons. By the intense heat of the solar rays in the focus of a powerful lens, it is volatilized. Macquer thus condensed its vapour on a plate of polished silver held above the gold in the focus of the mirror; and Lavoisier found it to be volatilized by the heat excited by a stream of oxygen gas directed on burning charcoal.

It has been supposed, that gold is incapable of oxidation by the action of heat and air. Boyle and Kunckel kept it exposed for months in a state of fusion to a violent heat, without finding it to undergo any change; and as its oxide, obtained by the agency of an acid, is reduced to the metallic state, by a heat little higher than ignition, it has been inferred, that this precludes the possibility of the metal attracting oxygen at a high temperature. Berthollet remarks from this fact, that "it cannot be supposed that the action of heat, by being rendered more energetic, can produce an effect totally opposite[*]." In some experiments by Macquer, in which gold appeared to be oxidated when exposed on vessels of earthen ware to the heat of powerful burning-glasses, he supposes the effect to have been produced by the action of the earthy matter, promoting the oxidation, and the vitrification of the oxide.

On this subject, however, there is now no ambiguity; and the possibility of oxidating gold at a high temperature cannot be disputed. Gold leaf, inclosed between plates of glass, and subjected to a powerful electric discharge, is converted into a purple oxide. Van Marum caused it to burn by powerful electric sparks; and Cuthbertson found, that electric discharges, transmitted over a gold wire inclosed in a glass tube with atmospheric air, convert it into a powder of a brownish purple colour, while the air is diminished in volume, and rendered incapable of supporting combustion [†]. The combustion of gold is even vivid, when it is subjected to the action of a powerful galvanic battery; and it burns in the flame of an united stream of oxygen and hydrogen gases. In these cases, an intense heat suddenly applied to the metal, probably volatilizes it, and thus enables it to combine with oxygen, the oxide at the same time condensing, and being withdrawn from the high temperature; while a lower heat, gradually applied, would augment the elasticity of the oxygen gas, without proportionally diminishing the cohesion of the metal.

In conformity to the opinion of the difficult oxidation of

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[*] Chemical Statics, vol. ii. p. 511.

[†] Nicholson's Journal, vol. v. 4to, p. 146.

gold, it was supposed not to be effected by deflagration with nitre: and this process has been employed to free it from the baser metals with which it has been alloyed. Mr Tennant found, however, that in the experiment of heating the diamond with nitre in a gold tube, the tube was acted on; and on exposing gold with nitre to a red heat for three hours, a portion was oxidated and dissolved *.

It is difficult to determine the proportions in which gold combines with oxygen, owing to the great facility of decomposition of its oxides. Proust obtained results so discordant, as to assign the proportion from one experiment, of 100 of gold to 8.57 of oxygen, and in another to 31 †. Oberkampft, from the oxide precipitated from the solution of muriate of gold by an alkali, obtained, in its decomposition by heat, a quantity of oxygen equal to 10 to 100 of gold ‡. And the same proportion had been assigned by Bergman. From the experiments of Berzelius, two oxides of gold appear to be recognised of definite composition. When the metal is dissolved in nitro-muriatic acid, and the solution is evaporated to dryness, and heated until the dry mass begin to give out oxymuriatic gas, the product affords by solution in water a muriate, which appears to contain the metal at the maximum of oxidation. To determine its proportions, Berzelius decomposed it by metallic quicksilver, which attracts its oxygen; and from the quantity of quicksilver oxidated he inferred, that this peroxide is composed of 89.225 of gold, and 10.775 of oxygen, or that 100 of gold are combined with 12.077 of oxygen. When neutral muriate of gold is heated, it gives out oxymuriatic gas, and the residue consists of a straw coloured mass, which contains the metal in a low state of oxidation, the higher proportion of oxygen having been ab-

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* Philosophical Transactions, 1797.

† Journal de Physique, tom. lxii. p. 158. 159.

‡ Philosophical Magazine, vol. xliv. p. 415.

stracted in the production of the oxymuriatic acid. When this salt is acted on by boiling water, it is decomposed and resolved into metallic gold, and the salt at the maximum of oxidation; the latter, according to Berzelius, affords, when decomposed, a quantity of gold exactly half of the first quantity; hence the oxide in the per-muriate contains a quantity of oxygen three times larger than that in the other. In the latter, therefore, 100 of gold are combined with 4.026, or it is composed of gold 96.13, oxygen 3.87. These proportions in the two oxides lead to the conjecture, that an intermediate oxide exists, with 8 of oxygen, but it has not been clearly established. The protoxide, separated from its muriate by an alkali, is a powder of a bright green colour; the per-oxide is of a reddish-brown colour. They are both very susceptible of decomposition *. The oxygen is expelled, and the gold reduced to the metallic form, by an elevation of temperature not much superior to that of ignition.

The attraction of gold to oxygen is so weak, that it is scarcely acted on by the acids. It was supposed to be insoluble even in the nitric, or nitrous acid, which, in general, parts with oxygen with so much facility; and when gold leaf is put into the acid in the cold, it seems to suffer no change. When nitrous acid, however, is boiled on gold, it appears to be capable of dissolving a small portion of it. This was observed by Brandt, and was confirmed by Schoeffer and Bergman. It was afterwards made the subject of experiment by Tillet, who found, that by boiling nitrous acid on gold, the metal lost weight, which, however, in opposition even to the facts his experiments establish, he ascribed to the erosion and mechanical suspension of the gold, and not to its proper solution †. According to Deyeux, the gold is more readily dissolved,

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* Nicholson's Journal, vol. xxxvi. p. 347.

† Mémoires de l'Acad. des Sciences, 1780, p. 241.

when the acid is highly charged with nitric oxide. The quantity dissolved is so inconsiderable, and depends on such conditions, that the accuracy of the processes of assaying can scarcely be affected by it.

The proper solvent of gold is nitro-muriatic acid. The acid generally used, is that formed of two parts of nitric acid, and one of muriatic acid. Gold leaf put into it instantly disappears; and when poured on gold in mass, the solution is accompanied with an effervescence, from the disengagement of nitric oxide gas. The above proportion of nitric acid is often reduced to an equal part: from the experiments of Proust *, it appears, that an acid formed of even four parts of muriatic acid to one of nitric, dissolves more gold than where less of the former acid is used. Vauquelin, from experiments made with the view of determining the proper proportions, fixed them at two parts by weight of muriatic acid, and one of nitric acid †.

As gold is soluble in oxymuriatic acid, and as a portion of this acid is formed by the reciprocal action of nitric and muriatic acids, it has been supposed, that its solution in the nitro-muriatic depends on the presence of the oxy-muriatic acid. But it is dissolved more rapidly, and in larger quantity, than it is by oxymuriatic acid in any state of condensation; the probable theory of the operation, therefore, is that given by Berthollet, that the muriatic acid, by a disposing or resulting affinity, enables the gold to attract oxygen from the nitric acid, and then combines with the oxide of gold; the operation being similar to that by which an acid facilitates the oxidation and solution of a metal, by enabling it to decompose water. Muriatic acid must exert such an affinity; and it appears from the facts above stated, with regard to the action of nitric acid on gold, that the addition of a weak force will enable the

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* Nicholson's Journal, vol. xiv. p. 238.

† Ibid. vol. xxx. p. 249.

gold to decompose that acid. Accordingly, the combination is principally a muriate of gold, as the oxidation of the metal can proceed only while the affinity of the muriatic acid aids it. For the same reason it is difficult to obtain a solution without an excess of acid. Strictly speaking, too, the solution is a nitro-muriate, or the nitric acid exerts an action on the metallic oxide, as well as the muriatic acid; and it is only by evaporation and crystallization, that the proper muriate of gold is obtained.

The solution, when the compound acid has dissolved as much of the gold as it can do, is of a rich yellow colour; according to Oberkampft, however, this is owing to excess of acid; when exposed to heat to dissipate this, it becomes of a brownish red colour; and when neutralized by an alkali, it becomes red. The yellow solution is corrosive, and communicates to animal membrane a purple tinge. By evaporation, crystals of muriate of gold are obtained of a rich yellow colour, in the form of prisms, or in single or double tetrahedral pyramids. This salt, Berzelius states, is a super-muriate; it is deliquescent; is soluble in water, and in alkohol and ether: it is deprived by heat of its excess of acid and water of crystallization, and forms a mass of a deep ruby colour, which with water forms a red solution.

A similar combination is formed by the action of oxymuriatic acid on gold. The solution, however, is slow, and no large quantity of gold can be dissolved; but it contains less excess of acid. In oxymuriatic acid gas, gold leaf is instantly fused, and dissolved.

Although gold cannot be dissolved by the other acids, its oxides may be combined with them. Few of its salts have been examined. According to Gren, the sulphate and nitrate do not crystallize. The phosphate may be fused, and forms a glass of a fine red colour. Nitric acid, instead of combining with its oxide rapidly, as it does with the greater number of oxides, dissolves it slowly.

The solution of gold in nitro-muriatic acid is decomposed by the alkalis, but with results which are not uniform, and with regard to which, therefore, the statements have been very discordant. Potash, it is generally stated, throws down a precipitate of a yellow colour, which varies according to the state of the solution with regard to dilution, and the quantity of alkali used, and frequently is more or less violet. It is not easy to precipitate the whole of the gold; and if an excess of alkali be added, part of the precipitate is re-dissolved. Proust has remarked, that part of the gold is precipitated in its metallic state, and that this may be discovered by adding muriatic acid to the precipitate, which dissolves the oxide, leaving the metallic gold undissolved *. According to Vauquelin, however, neither potash nor soda (and he adds also barytes and lime) precipitates the solution of muriate of gold in the cold; the alkalis only deepen the colour; but at a boiling heat, a precipitate of a red colour is thrown down; the quantity of this is much diminished if the alkali be even slightly in excess. After all the oxide which potash can precipitate has been thrown down, the liquor is colourless; but the addition of a little muriatic acid restores its yellow colour, and a portion of gold is thrown down from it by green sulphate of iron †. Oberkampft states, that on pouring muriate of gold into a solution of potash, leaving the latter in excess, an inconsiderable precipitate is formed of a blackish grey colour, which is increased by heat. With less excess of alkali, precipitates of a yellow, or reddish yellow colour, are formed. And if the alkali is added to the solution of gold, taking care not to exceed the point of saturation, a yellow precipitate is formed. The black precipitate he found to be a pure oxide, the yellow precipitates retained portions of acid in combina-

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* Nicholson's Journal, vol. xv. p. 245.

† Ibid. vol. xxx. p. 255.

tion. The alkaline earths produce similar results. The precipitates which potash and soda afford by the aid of heat, were supposed by Vauquelin to be the pure oxide; he found them to have a styptic taste, and to be soluble in water; but these qualities arise from the presence of the acid they contain. The alkalis, on the other hand, never throw down the whole oxide from the solutions of gold, but form with it and the acids soluble ternary compounds; and hence, if there has been much excess of acid in the solution, very little precipitation takes place[*]. This, however, has been denied by Figuier, who finds the quantities to be the same[†].

The action of ammonia on muriate of gold is more peculiar; it affords a precipitate which is highly fulminating, Aurum Fulminans, or Fulminating Gold, and which, being one of the first chemical preparations possessing this property known to chemists, has much engaged their attention. It was known even to the alchemists. To a solution of gold in nitro-muriatic acid, diluted with three or four times its weight of water, liquid ammonia is added, as long as any precipitate is thrown down, taking care not to add an excess of alkali, as part of the precipitate would be re-dissolved. The precipitate, after being washed with water, is allowed to dry by exposure to the air, avoiding the application of heat. It is of a reddish yellow colour, and weighs about one-fourth more than the gold employed. A similar preparation may be obtained by dissolving gold in nitro-muriatic acid, prepared by adding muriate of ammonia to nitric acid, and decomposing the solution by potash; or by precipitating oxide of gold from its solution by a fixed alkali, and afterwards digesting it in ammonia.

Its detonation is occasioned by heat, or by friction, or percussion. The temperature requisite is, according to

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[*] Oberkampft, Philosophical Magazine, vol. xliv. p. 412.

[†] Annales de Chimie et Physique, tom. ii. p. 102.

Bergman, between 120° and 300: it explodes with an acute report, and an obscure flash: if exploded on a metallic plate in the quantity of 10 or 12 grains, it perforates or lacerates it: in smaller quantity it depresses it. By friction in a mortar, or even by a slighter agitation, its explosion is also occasioned; and this has sometimes been the cause of unfortunate accidents. One occurred in the presence of Macquer: a person having put a quantity of it into a phial, with a glass-stopper, and not observing that a little had adhered to the neck of the phial, on turning round the stopper, caused this to explode: the explosion was probably communicated to the quantity in the phial, as the person was thrown to a distance with violence, and rendered blind, by the minute splinters of glass having struck both eyes.

The detonating power is much lessened by interposing between the particles of the fulminating gold any uninflammable matter, as by mixing with it a little of any of the fixed alkalis or earths. Sulphur removes it, so that the mixture burns merely with a slight deflagration. Oils have the same power. The acids, at least the diluted sulphuric and the nitric, do not decompose it even with the assistance of heat, as it still detonates as before: nor does water boiled on it impair its detonating power. Muriatic acid, however, dissolves a portion of the oxide of gold, and thus alters the composition.

Experiments have been made with caution, with the view of discovering the cause of the detonating quality of this substance. By exploding small portions of it in close glass-vessels, a powder of a purple colour is obtained, with which are intermixed particles of reduced gold: and if the experiment be performed so as to collect any aërial product, an elastic fluid is disengaged, which Bergman found to be nitrogen gas. He observed also, that by heating it very gradually, it suffered decomposition without detonation, as it did also when heat was applied to it under pressure, in close metallic vessels. He farther found, that the use of ammonia in the preparation is necessary; and that it is a compound of ammonia and oxide of gold *. In its formation, therefore, one portion of the ammonia must saturate the acid; and the oxide of gold, separated from its combination, must attract another portion of the ammonia, forming the precipitate. Its detonation Bergman ascribed to the re-action of its principles at a high temperature, and the consequent disengagement of elastic products; the oxygen of the oxide attracts the hydrogen of the ammonia, forming watery vapour; the nitrogen assumes the elastic form; and the elasticity of both is augmented by the high temperature: and accordingly, by detonating in a copper tube, Berthollet found nitrogen gas to be disengaged; a few drops of water condensed at the extremity of the tube; and the gold was reduced to the metallic state. These new combinations take place with rapidity, either from heat or friction, principally from the weak affinity with which oxygen is retained by gold. Gren supposed that the fulminating gold contains muriatic acid; that when heated, this attracts the oxygen of the oxide, passes to the state of oxymuriatic, or perhaps hyper-oxymuriatic acid, which re-acts on the ammonia;—an hypothesis not improbable, from the consideration that metallic precipitates frequently retain a portion of the acid with which the metallic oxide had been combined. Proust found 100 parts of fulminating gold to yield 73 of pure gold.

Muriate of gold is decomposed by a number of agents, which expell or attract its oxygen. It is reduced to the metallic state by the chemical agency of light, and of inflammable bodies, as is exemplified in the experiments of Mrs Fulhame already referred to. A piece of silk dipt in a dilute solution of it, moistened with water, and exposed to the rays of the sun, is soon covered with reduced gold:

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* Physical and Chemical Essays, vol. ii. p. 124.

and a similar appearance is produced on exposing the silk to hydrogen gas, to sulphurous acid gas, to a solution of phosphorus in ether, or to an alkaline solution of charcoal. Phosphorus immersed in the solution of muriate of gold, precipitates the metal.

The greater number of the metals likewise decompose it. Copper, iron, and zinc, throw down the gold in its metallic state; other metals, as silver, or lead, precipitate it in the state of the purple oxide. A precipitate of this kind by tin, known by the name of Purple Powder of Cassius, is valued for the beauty of the colour it gives to glass or enamel. It may be obtained by various processes, and even simply by immersing a plate of tin in a dilute solution of muriate of gold; but that generally followed when it is prepared for the above use, is to dissolve pure gold in nitro-muriatic acid; and to prepare a solution of tin, by dissolving the metal in small portions at a time, without the application of heat, in an acid composed of two parts of nitric, and one of muriatic acid, previously diluted with an equal weight of water. This solution, after it has attained saturation, is largely diluted: and to this the solution of gold, in quantity equal to half the quantity of solution of tin, is added: the liquor becomes of a purplish red colour, and a precipitate subsides, which is washed and dried. It is the only known preparation which gives a pure and rich red colour to glass.

It was always found difficult to obtain the precipitate uniform in colour; and the theory of the process was not well understood. Pelletier shewed that it is a compound of oxides of tin and gold, and that its formation is owing to the strong attraction of tin to oxygen, and the large quantity with which it is disposed to combine. When the two solutions are mixed, the oxide of tin, which is nearly at the minimum of oxidation, attracts part of the oxygen of the oxide of gold: the two oxides, thus brought to states of oxidation different from those in which they existed in the separate solutions, and probably likewise exerting mutual affinities, are no longer soluble, and are precipitated in combination. This points out the circumstances required to be attended to in the process to obtain the preparation uniform: the whole depends on having the solution of tin at the *minimum* of oxidation, or as nearly so as possible; and hence it must be prepared slowly, without the application of heat, and must be used newly prepared, as otherwise the tin passes to too highly an oxidated state. The proportions, too, are very variable, according to the concentration of the solutions. Proust has maintained, that the gold exists in the metallic state, united with the oxide of tin. Oberkampft remarks, that it appears, at least, to be very slightly oxidated, and if the solutions are very concentrated, metallic gold is always thrown down.

This purple powder is scarcely acted on by nitric or muriatic acid; when boiled on it, they abstract only a little oxide of tin; by the nitro-muriatic, the oxide of gold is dissolved, leaving the greater part of the oxide of tin. Liquid ammonia dissolves it entirely *.

Muriate of gold is decomposed by other metallic salts, the oxides of which attract its oxygen, and those which have a great tendency to a high state of oxidation, are capable even of attracting the whole oxygen. Thus, a solution of green sulphate of iron added to the solution of muriate of gold, precipitates the gold in the metallic state, while the iron passes to the state of the red sulphate. From the purplish colour which the precipitate has, it probably contains a portion of oxide; and accordingly Proust affirms, that muriatic or nitric acid dissolves a little of it. This has been regarded as the best re-agent to discover gold, and also as affording the best process for obtaining gold pure; but silver is precipitated in a similar

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* Proust, Journal de Physique, tom. lxii.; or Nicholson's Journal, vol. xv. p. 245.

manner, so that, if the gold be alloyed with it, it will not be separated.

Muriate of gold is gradually decomposed by ether, or by volatile oils. On mixing them with its solution, the muriate is at first dissolved, and is separated from the watery part. This solution is even soluble in alkohol, and such liquids formed the different kinds of what was formerly named Potable Gold; which, when gold was supposed to possess medicinal powers, were, from their mildness, sometimes taken internally. After some time, the gold is precipitated in its metallic state; the oxygen combined with it in the muriate, being attracted by the carbon or the hydrogen of the ether or oil.

When a current of hydrogen gas is transmitted through a dilute solution of muriate of gold, the liquor assumes a fine purple-red colour; and after some time, a very light precipitate subsides, which appears to be metallic gold in a state of extreme division. It is not acted on by muriatic acid, but nitro-muriatic acid dissolves it speedily.

Gold does not combine with sulphur by fusion; but the sulphuret is formed by the action of sulphuretted hydrogen gas, passed through a solution of muriate of gold. It is a precipitate of a black colour. Proust supposed this to be a mixture of sulphur and metallic gold. But Oberkampft found, that even after agitation in water, it remains perfectly homogeneous; and is a sulphuret, though the combination is slight, and the sulphur is easily expelled by heat. According to his analysis, it consists of 80.39 of gold, and sulphur 19.61. 100 of gold, therefore, combine with 24.39 of sulphur, a result which, from the equivalent combining weights of sulphur and oxygen, corresponds sufficiently with the proportion of oxygen in the peroxide assigned by Berzelius. The alkaline hydro-sulphurets throw down from muriate of gold a black precipitate, similar to that formed by sulphuretted hydrogen; but when they are more or less sulphuretted, the precipitate contains more or less sulphur in excess, and the colour is more or less deep. Hydro-sulphuret of potash dissolves sulphuret of gold, and gives it a reddish yellow colour: acids added to this solution, cause the metallic sulphuret to re-appear by saturating the potash, and disengaging the sulphuretted hydrogen. Sulphuret of gold treated with potash, becomes yellow, and a portion is dissolved, yielding a solution less deeply coloured, which, with the acids, exhibits the same phenomena. On this depends a result, which appeared extraordinary to the older chemists, and attracted much of their notice, that metallic gold is rendered soluble in water by the medium of sulphur and an alkali. If sulphuret of potash is fused with one-eighth of its weight of gold leaf, the compound is dissolved by water, forming a solution of a green colour, which is decomposed by acids. Gold does not dissolve in the hydro-sulphurets, but only by the addition of sulphur, with the assistance of heat *.

Gold combines with phosphorus, either by the process of Pelletier, already described, or by projecting small pieces of phosphorus on melted gold. The compound is of a white colour, and brittle; it contains only a small proportion of phosphorus, according to Pelletier, not more than a twenty-fourth of its weight. It is fusible: when heated in atmospheric air it is decomposed, the phosphorus burning at its surface. If phosphuretted hydrogen be transmitted through a dilute solution of muriate of gold, the colour soon passes to a deep purple; if the addition of the gas be then stopt, a precipitate forms slowly, which, according to Oberkampft, is metallic gold. But if the transmission of the gas be continued, the gold, in this state of extreme division, appears to attract phosphorus from it, and a phosphuret is precipitated of a black colour.

Gold forms alloys with the greater number of the metals. An extensive series of experiments on these was made by

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* Oberkampft, Philosophical Magazine, vol. xliv. p. 410.

Mr Hatchet, with a view of determining the principal facts with regard to the use of gold as coin *, of which it will be sufficient to give a brief abstract; as any of these alloys of importance will be noticed under the history of the other metals.

All the metals, with the exception of silver, platina, and copper, in combining with gold, impair greatly either its ductility or its colour. Bismuth, lead, and antimony, are those which render it most brittle. The alloy with platina is of a yellowish white colour, very ductile, heavy, and elastic when hammered. The alloy with silver in the standard proportion, or 1 in 12, approaches the nearest to the ductility of fine gold of any alloy, and its specific gravity differs little from the mean specific gravity of the respective metals. When the silver amounts to one-fifth, the colour approaches to green, and forms what is called green gold. Gold, in combination with copper, has its colour rather heightened than impaired: its hardness is increased, and its ductility little lessened, when the standard proportion of 1 part in 12 is not exceeded. Hence this alloy of 22 carats fine, is generally used when gold is fabricated into plate or ornaments, and also forms the gold coin of this country. A very small portion either of lead or antimony in the copper, impairs much the ductility of the alloy; and as both these metals are often associated with copper in its ores, and remain in the copper of commerce, the brittleness sometimes communicated to gold by copper, must arise from their operation. One ounce of copper, Hatchet found, might contain four grains either of antimony or lead, without any apparent change of colour or ductility; but if such copper were used to alloy gold, one ounce of it being added to eleven ounces, the ductility is destroyed. With quicksilver gold unites with great facility. If the surface of the gold be merely touched with it, it be-

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* Philosophical Transactions, 1803.

comes white; its substance is soon penetrated so as to become brittle, and at length is completely dissolved. The amalgam is of a yellow colour, and, if the proportion of gold be large, is solid and crystallizable. If heated in atmospheric air, both metals are oxidated. The alloy with iron is harder than gold, very ductile and malleable; but the colour is debased to a yellowish grey. Tin was supposed, even in the most minute quantity, to render gold extremely brittle. This was shewn to be a mistake by Mr Alchorne, and the effect must have arisen from tin frequently containing antimony, lead, bismuth, or zinc. A large proportion, as 1-10th, impairs the ductility, and renders the colour pale; but a small quantity, as 1-30th, does no material injury. Zinc is injurious to the ductility of gold. Lead, bismuth, and antimony, even in very small quantity, render it very brittle, and diminish its brilliancy and the deepness of its colour: less than one quarter of a grain to an ounce gives rise to brittleness, and even the vapour arising from these metals in fusion, produces these changes. The colour and ductility are less injured by nickel. Cobalt is more injurious, as are also manganese and arsenic. The alloy with manganese is less fusible than pure gold: that with arsenic is very fusible, hard, and of a grey colour.

Gold is applied to many useful and ornamental purposes. It is used as the principal medium of exchange. When perfectly pure, it is not so fit for coin, from its softness; in consequence of which the impression is soon obliterated, and it sustains loss from friction; hence it is alloyed to give it hardness. The metals that have been used for this purpose, are silver or copper. The alloy with the former is very ductile, but it is scarcely sufficiently hard, and the colour is too pale. That with copper is of a deeper colour, and is harder; while it is sufficiently ductile, if the copper has been pure. Gold made standard by a mixture of equal parts of silver and copper, has a colour approaching more to that of pure gold than any other alloy: this colour also remains uniform, while that of copper, after a certain degree of wear, becomes unequal *. This alloy appears also to suffer less from friction; but though it has these advantages, it does not appear, from Mr Hatchet's inquiries, that they are sufficient to compensate for the additional expence of the silver, especially as the gold brought to the mint generally contains a little of this metal, which renders the addition less necessary. Mr Hatchet subjected the different alloys that have been used as coin to friction, as similar as possible to that to which they must be subjected in the course of circulation. The loss was not considerable; and it appeared as the general result, that the present standard gold, or alloy of one part of copper in 12, is the best, or at least as good as any that could be chosen. If the copper be in larger proportion, more loss s sustained from friction.

The same alloy is employed in the fabrication of plate, and of trinkets, and lace; and, by other additions, various shades of colour are obtained. Its alloy, with a fifth part of silver, forms the green gold of the jewellers; and the addition of iron gives a blue tint.

By gilding, other metals receive a coating of gold, more

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* The cause of this is explained by Mr Hatchet. The gold, after being cast into coin, requires to be annealed; and in this process, when it has an alloy of copper, it acquires a black or brown colour, from the oxidation of the copper at the surface. This is removed by washing with a solution of alum. The effect of this is to remove the oxide of copper; and thus the surface of the coin is a film of pure gold. In the course of circulation, this is worn off, especially on the prominent parts; the colour of the alloy, which is deeper than that of pure gold, appears; and hence the unequal copper-like colour which coin that has been in circulation exhibits.

or less perfect, according to the method that is employed. The most substantial gilding is that effected by the medium of quicksilver on silver or copper. An amalgam is prepared of one part of gold, and eight of quicksilver: the surface of the metal to be gilt, is cleansed by very dilute nitric acid, and is brushed over with a dilute solution of quicksilver in that acid, so that a thin film of this metal adheres to the surface: the amalgam is then applied, as equally as possible, by a wire brush. The metal is exposed to heat over a charcoal fire: the quicksilver is volatilized, leaving a thin coating of gold: this is repeated to render the covering sufficiently uniform; the surface is lastly covered with a composition of wax, bole, alum, acetate of copper, and sulphate of copper; it is exposed to a red heat to melt this off; by this its colour is heightened: it is then burnished. Less substantial gilding is executed by dipping the metal in a mixed solution of muriate of gold, and corrosive muriate of mercury, and when dry exposing it to a red heat; or by macerating linen rags in a solution of muriate of gold; burning them to tinder; and rubbing this by a piece of cork strongly on the surface of the polished metal, afterwards applying the burnisher. Iron or steel is gilt either by merely applying gold leaf to the metal, the surface of which has been well cleansed and heated, the surface being burnished, and this being repeated according as the gilding is required to be more or less durable; or by diluting the solution of gold in nitro-muriatic acid with alkohol, and applying it to the clean surface. This last process has been improved by Mr Stoddart. A saturated solution of gold in nitro-muriatic acid being mixed with three times its weight of sulphuric ether, this dissolves the muriate of gold, and the solution is separated from the acid beneath. To gild the steel it is merely requisite to dip it, the surface being previously well polished and cleansed, in the ethereal solution, for an instant; and on withdrawing it, to wash it instantly by agitation in water *. Alkohol does as well as ether, and is more economical.

Gold leaf affords another mode of applying this metal. It has generally been supposed, that in making gold leaf the metal is employed pure: it would, however, be too soft and ductile to be uniformly extended. It is therefore hardened with from 3 to 12 grains of alloy in the ounce, silver or copper, or both, being used to form various shades of colour. The extension of it is performed by beating, after it has been brought to a certain degree of thinness, between pieces of animal membrane, on a polished anvil, with a polished hammer. The thickness of the leaf is about one two hundred and eighty-two thousandth part of an inch †. It is applied to wood by an adhesive size or glue, or sometimes by drying oil; to paper by the medium of a composition of the white of an egg, with sugar-candy, and a little bole. Glass is gilded by wetting the part with a solution of borax, applying gold leaf, and fixing it by burning; and porcelain is painted with gold, by mixing the powder obtained by evaporating the solution of muriate of gold to dryness with borax and a solution of gum, applying this by a pencil, and burning it in by the requisite heat.

Various tints of colour are given by the oxides of gold to glass and enamel. A rich red is communicated by the powder of Cassius; and even the fulminating gold has been applied to the same use.

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* Nicholson's Journal, vol. xi. p. 215.

† Ibid. 4to, vol. i. p. 133.

CHAP. II.

SILVER.

Silver is connected with gold, both by physical and chemical qualities. It has great ductility and malleability, considerable lustre and specific gravity; it is with difficulty oxidated by the joint action of heat and air; and its oxides, obtained by other processes, are like those of gold reduced by the action of heat alone. These qualities, the beauty of its colour, and its comparative scarcity, have rendered it the medium of exchange next in value to gold.

Silver exists native, and also mineralized, combined with sulphur, oxygen, muriatic and sulphuric acids, forming a number of ores. Besides the proper ores of silver, there are a number of metallic ores which contain it in small quantity, but often sufficiently great to render its extraction profitable: such are the grey copper ore, and some lead, cobalt, and arsenical ores.

Silver when native, is separated from the earthy matter by washing, and amalgamation with mercury; the latter being afterwards separated by distillation. When alloyed with antimony, or arsenic, or when mineralized, the ore is roasted to expel these metals, as well as the sulphur: and the residual matter is fused with lead, and refined by Cupellation, in a manner similar to that which has been described in the history of gold: the alloy of lead and silver being exposed to heat on the hearth of the refining furnace; the lead being oxidated with the foreign metals, the oxidation and vitrification of which it promotes; and the vitrified oxide being in part absorbed, and in part driven off by the blast of the bellows. The appearance of a vivid incandescence, or brightening, denotes when the silver has become pure. It retains a little gold in combination, but this does not alter its qualities, and the quantity is seldom such as to render its separation, by the operation of Parting, an object of importance. Some improvements have been made by Duhamel in the process of refining silver, particularly in constructing the refining vessel of sand and clay, instead of bone or wood ashes, which are not procured but at a considerable expence, and in the mode of withdrawing the vitrified oxide as it is formed, from the surface of the melted metal *. If the ore which is wrought contain only a small portion of silver, the previous operation of Eliquation is performed on it. This consists in adding a certain portion of lead to the metallic matter which remains after roasting and fusing the ore. This alloy is exposed to a degree of heat just sufficient to melt the lead, which runs out, and, from its affinity to the silver, carries it with it, leaving the copper, or other metals with which the silver had been combined. The alloy of silver and lead is then subjected to the usual refining process.

Silver has a colour more approaching to pure white than any other metal has; in lustre it is superior to gold; but it tarnishes from exposure to the air, not however from oxidation, but from the action of sulphuretted hydrogen, occasionally applied to its surface. Hence, it tarnishes more quickly in some situations than in others; and when it has been exposed for a number of years, scales of sulphuret of silver form on its surface. In malleability it is inferior only to gold. The finest silver-leaf is about the hundred and sixty thousandth of an inch thick, which is one-third thicker than gold-leaf. In ductility it is inferior to platina, and iron: but it possesses this property in an eminent degree; it may be drawn into wire extremely fine, and a wire of it, 1-10th inch diameter, supports, without

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* Nicholson's Journal, vol. xi. p. 206.

breaking, a weight of 270, or, as has been stated, 370 libs. It is harder than gold, is more elastic, and is peculiarly sonorous. Its specific gravity is 10.47, and is increased by hammering to 10.51.

Silver melts, according to Wedgwood, at 28° of his scale. Sir James Hall found its melting point to be not higher than 22°, measured by the pyrometer pieces that have been usually sold; and Guyton has stated it at 23°. When in fusion, its surface is extremely bright and luminous. By the usual method of allowing it to cool until it is congealed to some depth, then piercing the solid crust, and withdrawing the liquid part, it is obtained crystallized in octaedrons. In congealing it expands; hence the external crust, in the progress of the cooling, is burst by the expansion of the liquid within, and jets of silver raised. By a stronger heat, as that of a powerful lens, it is volatilized: it is even converted into vapour in the heat of a furnace; and it is volatilized in its combustion *.

Silver was believed to be equally difficult with gold of oxidation by the action of heat and air. Macquer, by exposing it in a crucible twenty times successively to the intense heat of a porcelain furnace, obtained, however, a small quantity of vitrified oxide. The electric discharge, transmitted through silver-leaf between two plates of glass, oxidates it, and vitrifies the oxide. Van Marum and Cuthbertson have found, that by passing the electric shock from a battery through a wire of silver, it is converted into an oxide of a blackish colour: a greenish flame appears at the moment of the discharge, and the oxygen of the air is consumed. By a powerful galvanic battery, silver-leaf is made to burn, emitting a beautiful green light; or with white light, if touched with charcoal at the extremity of the connecting galvanic wire. Lavoisier oxidated it by the heat excited by the flame of the blowpipe, urged by a stream of oxygen gas; and a fine wire of it burns in the

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* Vauquelin, Annales de Chimie, tom. lxxxix. p. 239.

kindled stream of oxygen and hydrogen gases. Its oxide is of an olive colour; it is decomposed by a high temperature, and the silver is reduced to the metallic state.

The degrees of oxidation of silver have not been well determined; indeed only one oxide is clearly recognized of uniform composition; that which exists in its saline compounds, and is obtained from the nitrate by the action of lime-water or barytic water. According to Proust, it is composed of 100 of metal, with 9.5 of oxygen. Davy states its composition at 100 of metal, with 7.3 of oxygen*; Berzelius at 100, with 7.92, inferred from the analysis of the muriate, or, as subsequently corrected from the analysis of sulphuret of silver, at 7.44, or 7.35†; and Gay Lussac, from the analysis of the muriate, at 7.6‡.

Silver is acted on by several of the acids. The sulphuric acid requires the assistance of a boiling heat; it is decomposed, sulphurous acid is disengaged, and sulphate of silver is formed with an excess of acid. Nitric acid acts upon it in the cold; but in this, as in some other cases, it is necessary to this action, that the acid should be diluted: if quite concentrated, the silver remains unaltered; but if a small quantity of water be added, the action commences, nitric oxide gas is discharged, from the partial abstraction of the oxygen of the acid, and the metal is dissolved in a quantity equal to about half the weight of the acid. Muriatic acid scarcely acts upon silver, but it is oxidated by oxymuriatic and nitro-muriatic acid. A number of facts with regard to its salts have been stated by Proust ||.

The sulphate is sparingly soluble in water. It is most readily formed by adding sulphuric acid to the solution of silver in nitric acid: the sulphate is precipitated. By boil-

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* Elements of Chemical Philosophy.

† Annals of Philosophy, vol. ii. p. 48. iii. p. 355.

‡ Recherches Physico-Chimiques, tom. ii. p. 120. 125.

|| Journal de Physique, tom. lxii. p. 211.

ing water upon it, a small quantity is dissolved; and on cooling needle-like crystals are deposited. It is blackened by exposure to light; and by a red heat is decomposed, its acid being expelled, and the metal reduced. Sulphurous acid may be combined with oxide of silver, by adding it to the solution of nitrate of silver; a precipitate is formed of a white powder, very sparingly soluble in water. According to Fourcroy, sulphite of silver is not blackened by light; it is decomposed by heat.

Nitrate of silver is obtained in solution by the action of diluted nitric acid upon silver. The liquor has at first a blue or green colour; when the silver is pure, this is owing to part of the nitric oxide arising from the decomposition of the acid being retained by the liquid; it soon disappears, and the solution is colourless. It remains permanently green, however, if the silver has contained any copper. If gold has been present, it falls down in a black powder. The solution, if the acid has been pure, is limpid: it is extremely caustic, first tinging any animal substance of a black colour, and consuming it if longer applied. When saturated, it shoots into brilliant white crystals in plates; easily soluble in water, and permanent in the air. They consist of 64 parts of oxide of silver, 22 of acid, and 14 of water: but according to Proust, this salt contains no water of crystallization; and consists of 69 or 70 of oxide of silver, with 31 or 30 of nitric acid. This salt is speedily blackened by exposure to light from a reduction of part of the metal: it is fused by a very moderate heat. When run into moulds so as to form small cylinders, it is the pharmaceutic preparation, known by the name of Lunar Caustic, which ought to receive the name of Sub-nitrate of Silver, as it is deprived of part of its acid in its fusion. It is the most powerful, and the most convenient in its use, of all the escharotics, giving less pain, and being more easily confined to the part to which it is applied. By continuing the application of heat to nitrate of silver after it is fused, it is decomposed, the nitric acid being expelled, and the silver partially reduced. It detonates with ignited charcoal, and is reduced. It detonates violently too, as Brugnatelli has shewn, when struck on an anvil with phosphorus; and if the hammer has been heated, it detonates even with sulphur. A nitrate of silver at the *minimum* of oxidation, more soluble than the other, much less disposed to crystallize, and differing considerably in its chemical relations from that at the *maximum* of oxidation, may be obtained, according to Proust, by boiling a solution of the common nitrate with metallic silver *.

Muriatic acid scarcely acts on silver: according to Proust, however, a portion of muriate is slowly formed, hydrogen gas being evolved. But when the acid, pure, or in any saline combination, is added to a solution of silver in nitric acid, it attracts the oxide, and the muriate of silver which is formed, being insoluble, is precipitated. By this agency it is the most delicate test of the presence of silver; and, on the other hand, nitrate of silver is the most delicate re-agent to discover muriatic acid. The muriate of silver is also formed by the action of nitro-muriatic acid; the nitric acid affording oxygen to the metal. It is likewise formed by the action of oxymuriatic acid; the metal, without inflaming in the gas, absorbing it. The precise determination of the composition of this compound is of much importance, as its formation is employed as the best mode of discovering the quantity of muriatic acid in other saline compounds. Wenzel, Proust, Chenevix, Zaboada, Bucholz, Rose, and Berthier, all agree in fixing the proportion of acid at from 17 to 18.3 in 100 of the dry muriate. Berzelius stated it at 81.3 of oxide, and 18.7 of acid †; Gay Lussac at 80.71, and 19.29 ‡; Dr

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* Nicholson's Journal, vol. xv. p. 376.

† Philosophical Magazine, vol. xli. p. 202.

‡ Recherches Physico-Chimiques, tom. ii. p. 125.

Marcet at 80.95, and 19.05; and Dr Wollaston has fixed it at these last proportions in his scale. According to the hypothesis of Gay Lussac and Davy, it is a chloride, and converting these last proportions conformable to this, its composition will be 75.6 of silver, and 24.4 of chlorine.

The neutral muriate is scarcely, if at all, soluble in water, hence its delicacy as a test in shewing the presence of muriatic acid. A slight degree of solubility is communicated to it by an excess of acid, and it is soluble to a certain extent in boiling concentrated solutions of other muriates, but mere dilution with water causes its precipitation. According to Proust, it is soluble in muriatic acid, and separates from it in octohedral crystals.

This salt is very sensible to the presence of light, being blackened in the course of one or two minutes exposure to the solar rays; from this property, it is the most sensible test of the intensity of the chemical agency of light. This blackening has been supposed to be owing to the partial reduction of the oxide, by the light expelling a portion of its oxygen. Scheele observed, that when the salt is placed under water, and exposed to the light, the water acquires a little acid. Berthollet has found, that the water acquires so much acid, as to redden litmus paper; a proof that it is not the oxymuriatic, but muriatic acid, that is disengaged; nor has he found any trace of the disengagement of oxygen. The blackening appears to be owing, therefore, to the partial disengagement of acid; it is produced likewise, as he has observed, by heat, muriate of silver becoming black before it enters into fusion, and a little muriatic acid without any oxygen being disengaged. And it appears to be effected even by the action of the air; as muriate of silver, exposed in a dark place to a current of air, became black *.

Muriate of silver is very fusible: from a gentle heat in

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* Chemical Statics, vol. i. p. 147.

a matrass it melts into a dense liquid: on cooling, it concretes into a substance of a pearl grey colour, semi-transparent, flexible, and malleable, which, from these properties, acquired from the older chemists the name of Luna Cornea, or Horn Silver. Octaedral crystals may be obtained from it by fusion. It is not volatile. By a higher temperature it is decomposed: both its acid and the oxygen of its oxide are expelled, and the metal is reduced and fused. This has been employed in practical chemistry, as the best method of obtaining pure silver; silver precipitated from its solution in nitric acid by muriatic acid, being pure; as copper, or other metals which may have been alloyed with it, remain in solution. The decomposition of the muriate by heat, is facilitated by the action of an alkali. Hence, in the process generally followed to obtain pure silver, one part of the muriate is mixed with four parts of sub-carbonate of potash, and the mixture is exposed to a full red heat in a large crucible, or, what is more secure, in a phial placed in sand in a crucible. After it has been brought into fusion, the crucible is removed, and allowed to cool slowly: a mass of pure silver is found at the bottom.

From the action of oxymuriatic acid on silver, we obtain a muriate, the oxygen serving to oxidate the metal. But Mr Chenevix found, that if a current of oxymuriatic gas be passed through oxide of silver suspended in water, a hyper-oxymuriate is formed. Another process by which he formed it is that of forming hyper-oxymuriate of alumina, by passing a current of oxymuriatic acid gas through water in which alumina is diffused: then digesting phosphate of silver with the hyper-oxymuriate of alumina, hyper-oxymuriate of silver is formed. Vauquelin finds, that it is formed by pouring chloric acid on oxide of silver newly precipitated, and still moist. It is abundantly soluble in water, dissolving, according to Vauquelin, in 10 or 12 parts of cold water, and requiring only two parts of hot water for its solution: this solution affords rhomboidal prisms on cooling, which are white and opaque. It is also soluble in alkohol. Exposed to heat, it is fused and decomposed, the excess of oxygen being given out. A grain or two of it, mixed with half its weight of sulphur, and struck, or rubbed, detonates with a loud report and a vivid flash *.

The combinations of silver with the other acids are, in general, sparingly soluble in water. They may be formed, by adding to the solution of silver in nitric acid, either the acid with which it is designed to combine the oxide of silver, or a neutral salt, into the composition of which that acid enters. The phosphate of silver prepared in this way, forms a dense white precipitate, which is not soluble in water, but may be dissolved in an excess of phosphoric acid. According to Berzelius, it is a subphosphate, the solutions of both salts, though neutral, leaving after the precipitation a liquor containing an excess of acid; it consists of 17 of phosphoric acid, and 83 of oxide of silver. It is fused by heat into a greenish opaque glass; when heated with charcoal, phosphuret of silver is formed. Carbonate of silver is in the form of a white powder, insoluble, which is blackened by light, and decomposed by heat, so as to afford pure silver. The fluate and borate are equally insoluble. Iodine combines with silver, and forms a mass insoluble in water. Hydriodate of silver is formed by adding a solution of an alkaline hydriodate to a solution of nitrate of silver; it forms a white precipitate. Oxiodate of potash added to nitrate of silver, forms a white precipitate, which is very soluble in ammonia †.

The saline compounds of silver are decomposed by the alkalis and earths. As the nitrate of silver, from its solu-

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* Philosophical Transactions, 1802, p. 162.

† Gay Lussac, Annales de Chimie, tom. xci. p. 67, 84.

bility, is best adapted to display the phenomena of these decompositions, it is principally with regard to it that they have been examined.

Potash added to its solution, throws down a precipitate varying in its colour, from a yellowish white to a brown or green, and probably a sub-nitrate. It is decomposed by heat, being reduced to metallic silver. Soda and lime exert a similar action. Ammonia occasions a precipitate of a grey colour, approaching to black, owing probably to the partial abstraction of oxygen from the oxide by the hydrogen of the ammonia. It possesses no fulminating property. Ammonia, however, has a strong tendency to react on oxide of silver, and combine with it; it forms a soluble compound; hence, a slight excess of ammonia added to the solution of silver, redissolves the precipitate, forming a purple salt, and the liquor acquires a brown colour.

A fulminating silver can be formed, composed of ammonia and oxide of silver, which is incomparably more powerful than fulminating gold. The process was discovered and described by Berthollet [*]. It consists in adding to a solution of nitrate of silver, lime-water: the precipitate formed is dried by exposure to the air for two or three days: it is then stirred in liquid ammonia: it thus assumes the form of a black powder, from which the liquor is to be poured off, and which is to be left to dry. This, according to Berthollet, is the fulminating silver. When the liquid, which has been decanted, is evaporated in a glass-vessel, it deposites, after it is cold, minute crystals: these detonate with the utmost violence: one of them being touched, is sufficient to burst the vessel with an explosion, and disperse the liquor. According to Dr Higgins, it is this crystallized matter which is the proper fulminating silver; and the black powder that is first deposited when the oxide of silver is stirred in the ammonia,

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[*] Journal de Physique, tom. xxxii. p. 475.

owes its detonating quality to the intermixture of a portion of it. This chemist has given more minute directions for preparing fulminating silver *; the process, as concisely described by Berthollet, having frequently not succeeded with chemists.

Such is the tendency of this preparation to detonation, that the slightest friction or percussion is sufficient to occasion it: it cannot be removed, nor even touched; the falling of a drop of water on it, or the accidental concussion of the vessel containing it, is sufficient to cause its explosion; and so violent is the explosion, that the experiment cannot be made with safety on a larger quantity than about a grain. Accidents have repeatedly happened from caution not having been observed with regard to it. One is related by Dr Higgins, in which a quantity of a strong solution of ammonia had been poured on the precipitated oxide of silver, and the vial corked. It had been agitated two or three times in the course of as many hours; after that, again agitating it, although no film had appeared on the surface, it exploded with the utmost violence, and the hand was impressed as by the blow of a large hammer. In making experiments with it, a mask, as Berthollet recommended, ought to be put on.

The theory given by Berthollet of the detonation of this preparation, is the same as that of fulminating gold. He regards it as a compound of ammonia and oxide of silver: the friction or percussion causes an approximation of the elastic principles; the oxygen of the oxide, and the hydrogen of the ammonia, instantly combine, forming watery vapour: the nitrogen assumes the elastic form; and the elasticity of both is augmented by the caloric set free. The greater detonating power of this preparation, compared with that of fulminating gold, is probably owing to oxide of silver containing a larger quantity of oxy-

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* Minutes of a Society for Philosophical Experiments, p. 344.

gen than oxide of gold does, and to this oxide attracting a larger portion of ammonia; so that a larger quantity of principles, disposed to enter into new combinations, and form elastic products, is contained in a given quantity.

Another fulminating silver has been described by Brugnatelli: 100 grains of fused sub-nitrate of silver, or lunar caustic, in powder, are put into a glass, one ounce of alkohol is poured on it, and then as much concentrated nitrous acid. The mixture becomes hot, with effervescence; it also becomes milky and opaque: distilled water must then be added to suspend the action; the white precipitate is collected on a filtre, and dried: it is the fulminating preparation. It resembles in its operation the fulminating quicksilver prepared by a similar process, discovered by Mr Howard, but more powerful. A grain of it thrown on burning fuel gives a loud report; and it detonates with violence when touched with a glass-rod that has been dipt in sulphuric acid *. A similar compound has been described by Descostils. It is prepared by dissolving silver in nitric acid, and pouring into the solution while it is going on a sufficient quantity of alkohol. An effervescence takes place, the liquor becomes turbid, a white crystalline powder falls down, which is removed when it ceases to increase, and is washed. Heat, percussion, or friction, causes it to explode with violence. Sulphuric acid inflames it. Muriatic and nitric acids decompose it. Ammonia dissolves it without changing its properties †.

According to the observations of Vauquelin, the alkalis do not decompose the muriate of silver. On boiling a solution of soda on muriate of silver, he did not find that any of the muriatic acid was attracted by the soda; and, on the contrary, oxide of silver newly precipitated from the solution in nitric acid, when thrown into a solution of

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* Nicholson's Journal, vol. vii. p. 285.

† Ibid. vol. xviii. p. 140.

muriate of soda, was converted into a soft curdled mass, exactly resembling muriate of silver formed in the common way; and the liquor above became alkaline. These effects seem to be partly owing to the influence of quantity on affinity; as a large portion of oxide of silver was found necessary to decompose the muriate of soda. The relation of muriate of silver to ammonia is also peculiar. Instead of being decomposed, a ternary combination is established, the product of which is soluble; hence liquid ammonia dissolves muriate of silver: the solution is at first colourless, but, when left exposed to the air, a pellicle of a grey or blue colour forms on its surface, which increases slowly and precipitates,—a change arising partly from the exhalation of the ammonia, and partly from its re-action on the oxide, which it partially reduces: octohedral crystals are also deposited.

The salts of silver are decomposed by the inflammables, and by the greater number of the other metals. These experiments have been made principally on the nitrate, as its solubility allows the affinities from which the decompositions arise to operate. Its watery solution is reduced by hydrogen gas, phosphorus, and other inflammables, when they are applied in the manner described under the history of gold. Charcoal immersed in the dilute solution, and exposed to the sun-beams, is coated with reduced silver. The decompositions by the metals are some of them partial, others complete,—differences arising not only from the different affinities of metals to oxygen, but from the affinity also exerted towards the silver. Iron, copper, and quicksilver, throw it down in the metallic state. The precipitation by iron appears, from the researches of Mr Keir *, to require that the silver should not be in a high state of oxidation, and there should be some excess of acid: a solution of green sulphate of iron likewise precipi-

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* Philosophical Transactions, 1790.

tates metallic silver. The precipitation by copper is easily effected; a plate of copper immersed in the nitrous solution, being instantly covered with a pellicle of reduced silver. This process is followed, in the art of assaying, to recover the silver which has been alloyed with gold, and which, in the operation of parting, has been dissolved by nitric acid; plates of copper being put into the solution, so as to precipitate the silver: it is also frequently employed to obtain silver free from other metals with which it has been alloyed. It is affirmed, however, by Proust, that this is attended with some loss, the whole of the silver not being thrown down. The silver precipitated has a small quantity of copper combined with it; but from this it may be freed by cupellation. This alloy of copper was supposed to arise from the exertion of an affinity between the two metals, but according to Vauquelin they are merely mixed together: the silver at first falls down pure, but as the operation proceeds, a portion of copper is thrown down with it, probably from the action of the hydrogen evolved by the galvanic action which occurs in the precipitation of metals. The precipitation of silver from its solution by quicksilver, when effected slowly, gives rise to a crystallized arrangement, similar in appearance to arborescence, and hence forming what the chemists named Arbor Dianæ. It may be effected by putting a little quicksilver into a dilute solution of nitrate of silver, but it is sooner obtained by the process given by Homberg; in which four parts of silver, with two of quicksilver, are dissolved in a sufficient quantity of diluted nitric acid, and diluted with forty-eight parts of distilled water. When a small piece of soft amalgam of silver is dropt into a little of this solution, in a short time filaments of reduced silver shoot from this, and extend upwards, giving the appearance of a shrub. This precipitation of the silver is occasioned by the quicksilver of the amalgam attracting its oxygen, favoured by the affinity of the one metal to the other, and probably by galvanic action, similar to what occurs in other cases of metallic precipitation and arborescence.

Silver combines easily with sulphur, when submitted in thin plates, imbedded in it, to such a heat as melts the sulphur. The sulphuret is of a deep violet colour, approaching to black; with a degree of metallic lustre; opaque, brittle, and soft. It is more fusible than the metal, and this in proportion to the quantity of sulphur combined in it. It is decomposed partially by heat. According to Berzelius, it is composed of 100 of silver, with 14.9 of sulphur. Sulphur appears also to be capable of combining with oxide of silver, at least such combinations exist in nature. Sulphuretted hydrogen gives to the surface of polished silver a violet tinge; and by continued exposure, a thin layer of sulphuret of silver is formed. The dark coloured precipitate thrown down by the solution of sulphuretted hydrogen, or of a hydro-sulphuret, from a solution of silver, is probably of a similar nature. The alkaline sulphurets, heated with silver, form a compound which is soluble in water, and from the solution of which the acids throw down sulphuret of silver.

Silver and phosphorus are capable of combining by the process of Pelletier, already described. The compound exceeds in weight the silver employed about one-fourth. It is white; of a granular texture; soft and brittle. It is decomposed partially by heat.

Silver enters into combination with the greater number of the metals: in these alloys, except that with gold, its ductility is generally impaired. The alloy with gold can be formed in various proportions, and according to these its properties vary. These proportions seem to be in some measure regulated by the difference in their specific gravity; for, according to an experiment related by Homberg, when the two metals in equal proportions are melted together, on allowing the alloy to cool and congeal, that part at the bottom of the mass is almost pure gold, or at least contains not more than about a seventh part of silver, while that at the top is nearly pure silver. When fused in other proportions, and cooled quickly, various alloys can be formed. The density is little increased by the combination, so that the specific gravities of the alloys differ little from those which, according to the calculation, would result from the relative proportions of the metals. The silver communicates hardness and elasticity to the gold, without much diminishing its ductility, but it impairs its colour greatly. From different proportions are obtained the pale yellow and the green gold of the goldsmiths. The alloy being more fusible than pure gold, is used in soldering this metal. The other alloys of silver will be noticed under the respective metals.

Silver is used as a medium of exchange, and to fabricate a variety of ornamental vessels. The applying it to the surface of copper or other metals, plating, as it is named, is performed in different modes. The most substantial is that of applying a thin plate of silver to a bar of copper perfectly clean, putting a little borax between them. The two, well bound together, are exposed to a red heat, the borax melts, and the silver adheres to the copper. The bar is then passed through the rolling press, and is thus extended. French plating is performed by applying leaves of silver successively to heated copper, and fixing them by burnishing. Another mode is to make silver into an amalgam with quicksilver, and the copper having been cleansed, and dipt in a dilute solution of quicksilver in nitric acid, the amalgam is applied to it; the plate is then heated, so as to volatilize the quicksilver, and favour the combination of the silver at the surface of the copper: it is afterwards burnished. Less durable silvering is effected by various methods, as by rubbing on the surface of the metal to be silvered, a mixture either of silver precipitated from its nitrous solution by copper, or of muriate of silver, with muriate of soda, and super-tartrate of potash, or a mixture of silver, precipitated by copper, with muriate of soda, muriate of ammonia, and a little corrosive muriate of mercury. The silver adheres to the surface of the copper, and the adhesion is rendered more permanent by the application of heat. By this last method, the scales of thermometers and barometers, and the dial-plates of clocks, are silvered.

It is an object of some importance, to recover the silver from plated goods which have been injured by wear. The process by eliquation and cupellation is too expensive. A method formerly in use, reviewed by Göettling [*], is to boil the plated metal in sulphuric acid, which oxidates and combines with the two metals. The sulphate of copper is separated by washing, and the sulphate of silver reduced. Mr Keir discovered a method now practised in this country, founded on a fact rather singular, which he observed, that a compound acid, formed of sulphuric and nitric acids, has the property of dissolving silver with facility, while it does not dissolve copper. The process which he recommended [†], is to dissolve one pound of nitre in eight or ten pounds of concentrated sulphuric acid with a moderate heat, in an earthen-glazed pan, adding to this liquor the plated copper in small pieces or shreds, stirring them frequently, so as to renew the surface, and assisting the mutual action by a heat of from 100° to 200° of Fahrenheit's scale. When the silver appears to be entirely dissolved from the copper, the liquor is to be poured off, the oxide of silver may be precipitated in the state of muriate of silver by the addition of muriate of soda, and this muriate may be reduced by the usual method: or, instead of these latter steps of the process, the solution of silver may be diluted with water; the diluted compound acid is capable of dissolving copper, though the concentrated is not:

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[*] Nicholson's Journal, vol. xi. p. 142.

[†] Philosophical Transactions, 1790.

in the dilute solution, therefore, copper plates may be immersed, and the silver will be precipitated in its metallic form. Mr Thomson has also pointed out an easy process for separating silver from copper, where the silver is in large proportion: it consists in exposing the metal in thin pieces, imbedded in powder of black oxide of manganese in a crucible, to a heat sufficient to melt silver: it is thus converted into an uniform black powder. This is mixed with three times its bulk of pounded green glass, and again exposed to a heat sufficient to melt the glass. On cooling, the silver is found at the bottom of the crucible perfectly pure, as the oxidated copper cannot be reduced, from no inflammable matter being present, while the high temperature is sufficient to reduce the silver alone. Gold may be purified by the same process *.

The solution of nitrate of silver is used in analytic chemistry, to discover the presence of muriatic acid in any state of combination. It is also employed, when much diluted, for marking linen which is to be bleached, forming what is named Indelible Ink, and for darkening the hair, and, as has been stated under the chemical history of light, for taking copies of paintings on glass.

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* Nicholson's Journal, vol. xi. p. 125.

CHAP. III.

PLATINA.

This metal, found principally in Peru, was unknown in Europe, until mention was made of it by Ulloa, in his relation of the voyage undertaken by the French Academicians to that country in 1735, to measure a degree of the meridian, with the view of determining the figure of the earth. Wood, an English metallurgist, brought a quantity of it from Jamaica in 1741, and gave an account of some of its properties. A more complete investigation of these was undertaken by Scheffer, and published in the Acts of the Academy of Sciences at Stockholm in 1753, and by Lewis, published in the Philosophical Transactions for 1754. Within these few years it has been more completely investigated; and not less than four distinct metals have been found associated with the metal to which the name of Platina properly belongs.

It had always been observed, that in dissolving crude platina in nitro-muriatic acid, a quantity of a black powder, amounting to about three parts in 100, remains undissolved. With regard to the nature of this, various conjectures had been formed. Descostils found that it afforded the oxide of a new metal *. Nearly about the same time, the discovery of this metal was made by Vauquelin †; and in this country by Mr Tennant ‡. The latter chemist, from the property which it has of exhibiting a strik-

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* Journal de Physique, tom. lvii. p. 384. Nicholson's Journal, vol. viii. p. 118.

† Annales de Chimie, tom. xlix. p. 188. 219. tom. l. p. 1.

‡ Philosophical Transactions, 1804, p. 411.

ing variety of colours, while dissolving in muriatic acid, gave it the name of *Iridium*. He also found, that another metal exists in the same black powder, and may be obtained by exposing it with soda, in a silver bason, to a red heat, a solution being obtained, on adding water, containing it in the state of an oxide in combination with the soda. From the pungent smell of its oxide, which is one of its most distinguishing characters, he gave it the name of *Osmium* *. Dr Wollaston, prosecuting these investigations, discovered other two metals in crude platina. A copious precipitate is formed when muriate of ammonia is added to its solution in nitro-muriatic acid. Dr Wollaston found, that after this precipitation is complete, there remains a portion of metallic matter in solution, which may be precipitated by immersing a plate of iron or zinc; and which consists chiefly of a peculiar metal, to which he gave the name of *Rhodium* †. He farther found, in the solution of crude platina in nitro-muriatic acid, another metal, which remains dissolved after the precipitation by muriate of ammonia, and the salt of which may be separated from rhodium by alkohol, or may be precipitated by prussiate of mercury. It is easily reduced by heat, and forms a metal of valuable qualities, to which he gave the name of *Palladium* ‡. All these metals form but a small proportion of crude platina; and their discovery exhibits, in a striking point of view, the delicacy and accuracy of chemical analysis. Their history may be given after that of platina.

Native Platina is brought from Peru; it has also been discovered by Vauquelin, in the ores of the mines of Guadalcanal in Spain, and more lately has been brought from Brazil. The Peruvian Platina is in small flattened grains, though pieces of a larger size have been found. Dr Wollaston has remarked, that of these grains some are harder

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* Philosophical Transactions, 1804, p. 416.

† Ibid. 1804, p. 419. ‡ Ibid. 1804, p. 426.

than the others; are not malleable; have a laminated structure; and are heavier, having a specific gravity equal to 19.5; while that of the softer grains is only 17.7; the former appears, from analysis, not to contain platina, but to be an alloy of iridium and osmium *. The crude platina is often mixed with other mineral substances, iron sand, gold in grains, fragments of hyacinth, &c. Besides these, the platina itself is alloyed; it is after fusion sensibly magnetic, from the presence of iron: and it is not certain whether the metals associated with it are in a state of combination, or whether any or all of them are merely interspersed among its grains. This renders it uncertain if we have an accurate knowledge of platina in a pure state; for although, in the processes by which it is purified, they are in part abstracted, they cannot be entirely removed. The Brazilian Platina appears to be less alloyed than the Peruvian with these other metals, and when freed indeed from grains of palladium mixed with it, to be platina free from rhodium and iridium, and nearly pure: and in the platina of Guadalcanal, none of the new metals of the Peruvian variety are found.

From the extreme infusibility of platina, its grains cannot be united by fusion, so as to obtain it in a dense mass: varions indirect processes have therefore been adopted.

De L'isle first succeeded in this by dissolving crude platina in nitro-muriatic acid, precipitating by muriate of ammonia, and exposing this precipitate, which is a muriate of ammonia and oxide of platina, to a very violent heat. The muriatic acid and ammonia are dissipated; the oxide of platina is reduced; and by pressing it while hot, the agglutination of the metal is rendered more perfect.

Margraaf observed, that by alloying platina with arsenic, it was rendered more fusible. This method was adopted with various modifications by several chemists;

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* Philosophical Transactions, 1805, p. 317.

and Jeannety of Paris succeeded by it in working platina into wire, plate, and vessels of different kinds, adapted chiefly to chemical purposes. A minute account of his process is given by Pelletier *.

Crude platina, in the quantity of a pound and a half, is mixed with three pounds of white arsenic, and one pound of subcarbonate of potash: and a third part of this mixture is thrown into a large crucible thoroughly ignited; after applying to this a strong heat, a second portion is thrown in, and afterwards the remaining portion, stirring the whole with a rod of platina. The heat is raised, and when the mass is melted, the crucible is allowed to cool. The metal thus obtained is magnetic: it is melted a second time: and if this does not free it sufficiently from iron, it is fused a third time. This first stage of the operation being finished, crucibles are taken, the bottom of which is flat: they are raised to a red heat, and into each is thrown a pound and a half of the metallic product, with an equal weight of arsenic, and half a pound of potash: the heat is raised so as to melt this, and the crucible is allowed to cool, placing it horizontally, so that the mass of metal shall be of equal thickness. The bars thus obtained are placed under a muffle, and being placed in a furnace, the fire is raised until they begin to exhale vapour; the doors of the furnace are then closed, to preserve the heat the same to the end. The bars are exposed to this heat for six hours. They are then put into common oil, and are exposed for the same length of time to a heat sufficient to dissipate the oil in vapour, and at the end the heat is pushed as far as it can be by the medium of the oil. The bars are cleansed with nitrous acid, and boiled in distilled water; they are then placed one above another in a crucible, and exposed to the strongest possible heat, and pressed down. They are lastly heated in the naked fire, and formed into a square bar, which is hammered for a longer or shorter time according to its

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* Mémoires de Chimie, tom. ii. p. 128.

size. This is on the whole the cheapest method of rendering platina malleable: but the metal is probably far from being pure.

Pelletier proposed to render platina fusible by exposing it to heat with phosphoric acid and charcoal, from which a phosphuret being formed, the phosphorus is afterwards burnt out; but it is difficult to separate the last portions of phosphorus; and the process has not been adopted by any artist *.

Another was given by Moussin Poushkin. The spongy metallic substance, obtained by reducing by heat the precipitate of platina from nitro-muriatic acid, is to be washed with boiling water; it is then to be boiled for half an hour in water mixed with one-tenth of muriatic acid, and after this is to be edulcorated and ignited. To one part of this metal, two parts of quicksilver are added, and they are to be amalgamated in a porphyry mortar; mixing them in small quantities at a time, and adding to the amalgam alternately small quantities of platina and mercury, until the whole quantities are combined. The amalgam is then to be quickly moulded in bars or plates, of at least half an inch in thickness, and of such a length as to be easily managed in the fire. Half an hour after they are formed, they begin to harden by the oxidation of the quicksilver. As soon as they have acquired the proper degree of hardness to be handled without breaking, they are to be placed in a furnace, and kept ignited under a muffle. The quicksilver is expelled, and the platina remains solid, so that after being strongly ignited two or three times before the bellows, it may be forged or laminated in the same manner as gold or silver †.

A simple process has been given by Mr Tilloch. It consists in exposing the precipitate from the solution of platina in nitro-muriatic acid, by muriate of ammonia, to

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* Memoires de Chimie, tom. ii. p. 152.

† Nicholson's Journal, vol. ix. p. 65.

a heat sufficient to volatilize the saline matter, and inclosing it after this in a piece of platina already malleable, and which has been spread out by the flatting mill. The envelope is exposed to a sufficient temperature, and, while hot, is cautiously hammered. This is repeated until it is obtained in a compact state *. Another by Ridolfi, is to fuse the crude platina with lead and sulphur, and afterwards hammer it at a white heat, so as to force out the lead and sulphur †.

Any of the preceding operations ought to be performed on the grains of crude platina, separated from the foreign substances usually mixed with them, by blowing obliquely a current of air on them by bellows: the lighter substances are separated, and the platina grains, from their greater weight, remain. The ore of iridium, which is mixed with the platina in grains very similar, ought also to be picked out. The separation, however, must be imperfect; and as iridium is dissolved by nitro-muriatic acid, and precipitated by muriate of ammonia, platina obtained from this precipitate must have an alloy of this metal. To avoid this, a process has been given by Descostils. It is very complicated, but the principal steps are to melt crude platina with zinc; and to submit the alloy to the action of sulphuric acid diluted with three parts of water, and when this ceases, to produce solution by adding fresh acid with the addition of a little nitric acid; the metal remaining after this operation dissolves easily in nitro-muriatic acid; this solution is evaporated to dryness: the dry matter is dissolved again in water, and carbonate of soda is added as long as any precipitation is produced. The liquid contains the triple salt of platina, soda, and muriatic acid, with a little iridium; by exposing it for some time to the air, the iridium separates, and the separation is rendered

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* Philosophical Magazine, vol. xxi. p. 175.

† Ibid. vol. xlviii. p. 72.

more complete by a moderate heat. The liquor filtered from the precipitate is lastly precipitated by muriate of ammonia; the precipitate, if it contain no iridium, is of a golden-yellow colour, and, reduced by heat, affords platina free from that metal, and, according to Descostils, in its state of greatest known purity *.

Platina, in the dense state into which it is brought by the usual processes, is of a white colour, approaching to that of silver, but having a shade of grey, with less lustre. In hardness, it is superior to the greater number of metals, and has been supposed to be exceeded only by manganese and iron. It can be beat into very thin plates: its ductility is very considerable, and, according to the experiments of Guyton †, is inferior only to that of iron and copper. According to Dr Wollaston's experiments, it must exceed much that of any other metal, a wire of platina being capable of extension by the method noticed under gold, so that its diameter is less than $\frac{1}{3000}$ of an inch, and by great care was reduced even in some specimens to $\frac{1}{30000}$. In specific gravity it exceeds all the metals, and is of course the heaviest substance with which we are acquainted. The specific gravity has been estimated so high as 23,000; according to Borda, it is 20,980; and according to Guyton, that of platina in wire is 20,847; it must vary as it has been more or less strongly hammered, and as it has been freed more or less completely from alloy.

Platina expands less by heat than the greater number of metals do. According to Borda, the expansion is equal to $\frac{1}{92000}$ for each degree of Reaumur, or $\frac{1}{110000}$ for each degree of the centigrade scale. According to Dr Wollaston, the expansion of steel between the freezing and boiling points of water, being estimated at twelve parts,

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* Memoires de la Societe d'Arcueil, tom. i. p. 370. Philosophical Magazine, vol. xxxvii. p. 65.

† Annales de Chimie, tom. xxv. p. 9.

that of platina is only nine. It is also a less perfect conductor of caloric than the other metals. Slips of silver, copper, and platina, being coated with wax, and one extremity being raised to a red heat, while the coating was melted on the silver to the distance of 3¼ inches, and on the copper to that of 2½, it was melted on the platina the length only of one inch *.

This metal, in relation to caloric, possesses a property peculiar to it and iron, that of *welding*, or softening at a temperature much below that which is requisite for its fusion; so that if in this state two pieces of it are compressed or beat, they may be united firmly.

Platina is one of the least fusible of the metals. The most intense heat which can be raised in a furnace, scarcely melts it: hence Guyton estimates its fusing point as beyond 160° of Wedgwood's pyrometer, or the extremity of the scale. Rose and Gehlen found, that in exposing platina to the intense heat in the furnace of the porcelain manufactory at Berlin, they could not fuse it, though the temperature was beyond that at which the pyrometrical pieces of Wedgwood cease to contract †. Mr Willis had however melted it, by exposing it to the heat of a wind furnace, imbedded in charcoal powder, and concluded that it can be brought into fusion at 150 of Wedgwood ‡: Guyton succeeded in melting it in small quantities, by exposing it to the heat of a blast furnace in a crucible with the aid of a flux of pounded glass, and charcoal ||: and Chenevix found it to be melted with the aid of borax in a crucible lined with charcoal powder, the crucible being exposed to the heat of a forge: But these results appear, from the researches of Descostils, to be owing to a small

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* Philosophical Transactions, 1805.

† Nicholson's Journal, vol. xi. p. 166.

‡ Manchester Memoirs, vol. iii. p. 467.

|| Fourcroy, vol. vi. p. 560.

portion of the charcoal, and by the intervention of this, part of the borax, or boracic acid, entering into combination with the metal; and accordingly it gains weight, and when dissolved, gives traces of boracic acid *. It is probably the base of the acid, or boron, which is combined with it, and gives it fusibility.

Though platina by itself is thus infusible, it may be melted in the focus of a very powerful burning lens, and in the heat excited in burning charcoal by oxygen gas, or that of a large galvanic battery.

Platina does not combine easily with oxygen. Its lustre, when it is free from alloy, is not diminished by exposure to air, even when it is exposed to a high heat. A wire of platina can be oxidated, however, by the electric discharge. Van Marum found, that a discharge transmitted over it from a powerful battery dissipated it in vapour, which condensed into a grey powder. Cuthbertson observed a similar production of oxide of a dark colour, and found the oxygen of the air to be abstracted. Mr Tennant observed, that platina heated with nitre is oxidated, and the oxide is combined with the alkali: on dissolving the saline matter, the greater part of the oxide is precipitated with a portion of alkali, forming a substance soluble in acids †.

No pure oxide of platina can be separated from its saline combinations, all the precipitates from its salts being triple compounds; and as it cannot be directly combined with oxygen, it is not easy to assign its degrees of oxidation. Chenevix inferred ‡, that an oxide afforded by decomposing the nitrate by heat, consists of 87 of metal and 13 of oxygen; in its reduction, he observed, that at one stage of the operation it became of a green colour, and this he supposed to constitute another oxide, containing about 7 of

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* Nicholson's Journal, vol. xxv. p. 66.

† Philosophical Transactions, 1797.

‡ Ibid. 1803. p. 314.

oxygen in 100 parts. Mr E. Davy repeated the experiments of Mr Chenevix without success. He employed a different method, reducing a solution of muriate of platina by hydrogen gas, finding the quantity of metallic platina deposited, and from the quantity of hydrogen absorbed, estimating the quantity of oxygen with which it must have been combined: the proportion thus found, was 84 of platina and 16 of oxygen. But in subsequent experiments, he gave as the composition of an oxide which is the base of sulphate of platina, the proportions of 89.1 of platina, and 10.9 of oxygen; and of an oxide, the base of fulminating platina, nearly the same, being 88.3 and 11.7 [*]. Berzelius assigned the compositions of two oxides of platina. That of the protoxide, he found by decomposing the muriate by heat, finding the quantity of oxymuriatic gas expelled, whence he could infer the quantity of oxygen, and finding at the same time the weight of the residue of metallic platina: the proportions thus determined, were 92.35 of platina, and 7.65 of oxygen. The quantity of oxygen in the peroxide, he found by the precipitation of platina by quicksilver, in the same manner as has been described with regard to gold; the proportions are 85.93 of platina, and 14.07 of oxygen. 100 of the metal, therefore, being combined in the one with 8.287, and in the other with 16.38 of oxygen [†]. Vauquelin still more lately has investigated this subject. He finds, that an oxide nearly pure may be procured by boiling a solution of soda, on what is called the insoluble muriate or sub-muriate, and that this oxide, from the quantity of oxygen expelled in its decomposition by heat, contains about 15 in 100 of oxygen. And in decomposing muriate of platina by quicksilver according to the method of Berzelius, he obtained between 15 and 16 as the

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[*] Philosophical Magazine, vol. xl. p. 269. 355.

[†] Annals of Philosophy, vol. v. p. 19.

proportion of oxygen. This proportion of oxygen, he remarks, is the same as that in which sulphur combines with platina, while in the other metallic sulphurets, the quantity of sulphur is, from the relative combining weights of these two elements, twice that of oxygen [*]. Still more lately Mr Cooper has inferred the existence of a protoxide of platina, in which 100 of metal are combined with 4.423 of oxygen. It is formed by precipitating a solution of muriate of platina by a solution of mercury; muriate of mercury is volatilized from the precipitate by a moderate heat, and the protoxide of platina remains in the form of a black powder, which may be reduced by a higher heat [†]. These various results leave a degree of uncertainty attached to this subject.

Although the soluble muriate of platina does not afford a pure oxide from the action of an alkali, Vauquelin regards that obtained from the sub-muriate as in this state. This oxide, or hydrated oxide rather, as he regards it, he describes as of a white colour, which becomes bluish-grey when exposed to light, and black when dried by heat. In this state, if heated farther, it gives out oxygen gas, losing 15 for 100 of its weight, and is reduced to metallic platina. Before exsiccation it dissolves in nitric acid without colouring it; but after having been dried, it does not dissolve.

Platina, from its weak attraction to oxygen, is acted on by none of the acids, the oxymuriatic and nitro-muriatic excepted. Sulphuric acid, in its concentrated state, boiled on it, does not alter it; even nitric acid boiled on it does not change its lustre; muriatic acid is equally inactive with regard to it. Its proper solvent is nitro-muriatic acid: this dissolves it with facility, especially when assisted by heat. According to Proust, an acid composed of

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[*] Annales de Chimie et Physique, tom. v. p. 264.

[†] Journal of the Royal Institution, vol. iii.

three parts of muriatic to one of nitric, dissolves the largest proportion of platina *. The solution is accompanied with a disengagement of nitric oxide, and nitrous acid vapour, with a smell of oxymuriatic acid ; and as it proceeds, a black powder is deposited, which is in part re-dissolved, if not removed. This consists partly of oxide of iridium, which, though by itself sparingly soluble in nitro-muriatic acid, becomes more soluble from the reciprocal action of platina, and partly of oxide of osmium ; and therefore does not appear with pure platina.

The solution, when it is concentrated, it of a dark reddish brown colour ; by evaporation it affords crystals of a similar colour. If as much metal has been employed as the acid can dissolve with the aid of heat, these seem to constitute the neutral muriate ; they are soluble, deliquescent, and acrid.

If the solution be evaporated to dryness, and heat be applied to the dry mass, oxymuriatic gas is discharged, the residue assumes a deep fawn brown colour, loses its taste, and becomes insoluble in water ; or at least remains so, after lixiviation with water to remove any adhering soluble muriate. It then forms what has been named insoluble muriate of platina. The same product, it was observed by Mr E. Davy, is obtained by digesting muriatic acid on platina, adding occasionally a little nitric acid, heating the dry mass cautiously nearly to redness, and afterwards boiling it with a considerable quantity of water. It remains in small masses of a dark olive brown or green colour, having neither smell nor taste, infusible, and nearly insoluble in water. The same substance appears from his experiments to be formed by the action of oxymuriatic acid gas on metallic platina. When heat is applied to promote this, the gas is slowly absorbed, and a substance is formed, passing through various shades of brown to olive ; but it

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* Philosophical Magazine, vol. xi. p. 122.

is difficult to render the combination complete, so as to bring the whole metal into this state *.

This substance is nearly insoluble in all the acids. The nitric, sulphuric, phosphoric, and acetic, have no effect on it at any temperature; it is scarcely affected by liquid muriatic acid at a common temperature, but when the acid is boiled on it, a portion is dissolved, and a solution of a yellowish brown colour is obtained. Strong nitro-muriatic acid appears to dissolve only a small portion of it. When boiled in a solution of pure potash or soda, a black powder is obtained, which, when decomposed by heat, furnishes oxygen and oxymuriatic gas. When digested in liquid ammonia it is partially dissolved, and the solution, when evaporated, leaves a film of metallic platina.

The properties and relations of this substance appear to prove, that it does not differ from the soluble muriate merely in the proportion of acid; the difference may therefore be inferred to depend on the degree of oxidation, and from analogy the insoluble muriate might be supposed to be at the lower degree of oxidation. This seems to be confirmed by the result, that when it is formed by heat from the soluble muriate, oxymuriatic gas is disengaged, as Vauquelin found; and also that, when dissolved by boiling in concentrated muriatic acid, it leaves undissolved, according to the same chemist, a portion of metallic platina †. Yet it is singular, that it is not much affected by oxymuriatic, or nitro-muriatic acid; and the oxide it contains seems to be at a high state of oxidation; it is possible, therefore, that the disengagement of oxymuriatic gas, in its formation from the soluble muriate, may be owing to the entire decomposition of a portion of the mass, leaving an intermixture of metallic platina. When exposed to a red heat in close vessels, it yields oxymuriatic gas and metallic pla-

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* Philosophical Magazine, vol. xl. p. 275.

† Annales de Chimie et Physique, tom. v. p. 264.

tina, in the proportion, Mr E. Davy found, of 27.5 of the former, and 72.5 of the latter [*]. Vauquelin found, that the soluble muriate, dried as far as possible without decomposition, afforded, when decomposed by a red heat, 47 hundredths of metallic platina; but he justly adds, that as it must undoubtedly have contained both free acid and water, no conclusion can be drawn with regard to its composition, compared with the other. The proportion of oxygen which he inferred to exist in the oxide of each, by the methods already stated, is almost the same; and although the insoluble muriate is not converted into the soluble one, by reagents which might be expected to communicate directly acid, or acid and oxygen, such as muriatic acid, oxymuriatic acid, or nitro-muriatic acid, yet Vauquelin found reason to conclude, that in some indirect processes this happens. In particular, in dissolving the precipitate which is formed from the mutual action of the muriatic solution of platina and nitrate of silver, and which contains the insoluble muriate, in muriatic acid, a solution of the soluble muriate is obtained. These results would seem to prove, that the difference of the two salts is in the proportion of acid.

The solution of muriate of platina is peculiarly distinguished by its relations to the alkaline bases. If potash be added in small quantity to the solution, as nearly neutral as possible, small octaedral crystals of a red colour are soon deposited; if the addition of the alkali be continued, a yellow powder is deposited, insoluble in water. No precipitation is produced, according to Margraaf and Lewis, by soda; but Bergman states, that by adding it in sufficient quantity, a yellow precipitate is thrown down. According to Vauquelin, however, it produces only a brown colour, without precipitation, and it is only by evaporating the liquor that crystals are formed. Ammonia gives readily a precipitate

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[*] Philosophical Magazine, vol. xl. p. 275.

in crystalline grains, which are of an octaedral form, of a red or reddish yellow colour; and when added in a larger quantity, another precipitate, in the form of a yellow powder. In all these precipitations, the pure oxide of platina is not thrown down; it has a tendency to form triple salts, by uniting with a portion of the acid and the alkali. These precipitates are therefore combinations of this kind. From this tendency to form ternary combinations, the same effects are produced on the solutions of platina by several neutral salts. Thus sulphate, nitrate, or muriate of potash, throws down a crystalline precipitate *, which is potassa-muriate of platina; muriate of soda digested with muriate of platina, or with nitric acid and metallic platina, affords large crystals of the soda-muriate; and muriate of ammonia, or even other ammoniacal salts, added to the solution of muriate of platina, produce, if it is not too much diluted, an immediate precipitate, from the formation of the ternary compound. All the salts, indeed, having potash or ammonia for their base, appear to form the same ternary compounds, by affording the potash or the ammonia to the muriate of platina.

Of these salts, the potassa-muriate of platina is in small octohedral crystals of a yellow colour, sparingly soluble in water. The ammoniaco-muriate is similar in appearance and general properties †. The soda-muriate is in crystals prismatic or tabular, and easily soluble ‡. Vauquelin has lately observed of this salt, that it is different in appearance, according as it is formed by adding muriate of soda to a neutral solution of muriate of platina, or by adding caustic soda to a solution of the muriate, and evaporating to crystallization,—the former being in regular crystals of an orange-red colour, the latter yielding crystalline plates of

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* Bergman's Essays, vol. ii. p. 169.

† Chenevix, Philosophical Transactions, 1804, p. 427.

‡ Journal de Physique, tom. lvii. p. 389.

a yellowish brown colour; and the solution of the former giving with muriate of ammonia a precipitate of a fine lemon-yellow colour, that of the latter a precipitate of a yellowish green. They are both, however, perfectly neutral; the proportion of their elements differs very little, that from the muriate of platina and soda containing a little more metal, the other more water, and probably a little more acid.

The effect of muriate of ammonia in precipitating the solution of platina in muriatic acid, was first observed by Lewis, and being a striking property of this metal, has always engaged the attention of chemists. There are some circumstances connected with it, particularly the colour of the precipitate, which have only been fully elucidated by the discoveries with regard to the metals naturally associated with platina.

It was known, that by adding, in successive portions, a concentrated solution of muriate of ammonia to a solution of platina in nitro-muriatic acid, precipitates of different colours are successively obtained. At first, the precipitate is of a *yellow* colour: if the liquor above it, which is still of a reddish brown colour, be poured off, and more muriate be added to it, the precipitate is of a *dark red* colour. These precipitates were supposed to differ from each other principally in the state of oxidation. Although partly connected with this, or with the state of combination, it appears from the experiments of Descostils *, and of Fourcroy and Vauquelin †, that the differences depend chiefly on the presence of iridium, the yellow precipitate consisting principally of oxide of platina, with a portion of ammonia and muriatic acid; while the other, the red precipitate, consists principally of the oxide of iridium, in a

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[*] Journal de Physique, tom. lvii. p. 386, &c.

[†] Annales de Chimie, tom. lxix. p. 204, &c.

similar state of ternary combination. The former, therefore, is afforded when pure platina is operated on.

The ammoniaco-muriate of platina, when exposed to a low red heat, is decomposed; the ammonia and the muriatic acid, partly in the state of oxymuriatic acid, are expelled; or with a slight variation of temperature, the ammonia is partly decomposed, and nitrogen, with water and muriatic acid, are disengaged. The platina is reduced to the metallic form.

The solution of muriate of platina is decomposed by several metallic salts. Muriate of tin is the most delicate test of it; a solution of platina so pale as hardly to be distinguished from water, assuming a bright red colour, by a single drop of the recent solution of tin in muriatic acid *. Green sulphate of iron, which precipitates gold and silver in their metallic form, was supposed not to precipitate platina; but Descostils found, that when the two solutions are boiled together, and there is no great excess of acid, the platina is copiously precipitated †. Nitrate of silver forms a precipitate, which consists of sub-muriate of platina and muriate of silver ‡.

The other salts of platina are imperfectly known. They have been supposed to be formed by dissolving the precipitate from the solution in nitro-muriatic acid by lime, in the acid with which it is intended to combine the platina. Mr Chenevix inferred, that the insoluble sulphate of platina, formed in this manner, consists of 54.5 of oxide, and 45.5 of acid and water; the insoluble muriate of 70 of oxide, and 30 of acid and water, and the sub-nitrate of 89 of oxide, and 11 of acid and water ||. But from the

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* Philosophical Transactions, 1805, p. 315.

† Nicholson's Journal, vol. xxv. p. 66.

‡ Vauquelin, Annales de Physique, tom. v. p. 269.

|| Philosophical Transactions, 1805, p. 315.

experiments of Mr E. Davy it appears, that no such compounds can be obtained. Lime causes a precipitate only in small quantity, and what is obtained is a ternary compound; neither can the solution of platina in nitro-muriatic acid, evaporated to dryness, be decomposed by heat, so as to leave an oxide soluble in other acids; nor can a nitrate be formed, by decomposing the muriate by nitrate of silver, for a precipitate is formed, composed of insoluble muriate of platina and muriate of silver. Even sulphuric acid, acting on the muriate or chloride with the aid of heat, does not expel the muriatic or oxymuriatic acid, and no sulphate therefore can be obtained in this mode.

A sulphate of platina, however, can be formed, which seems to have been first slightly noticed by Proust. It is obtained by the action of strong nitrous acid on the hydro-sulphuret of platina, precipitated by sulphuretted hydrogen from the muriate; on this substance, in a moist state, nitrous acid is digested, and at the end of the operation any excess of acid is driven off. The product is in form of a brittle porous mass, of a dark brown colour and brilliant, with a resinous lustre; its taste is metallic and caustic. It is deliquescent, and very soluble in water; it is also soluble in alkhol and ether. It is soluble in muriatic acid; and when boiled to dryness in this acid is decomposed, the insoluble muriate being formed. It is also soluble in nitric acid, but is not decomposed by it. It is decomposed when heated to redness in close vessels, a little oxygen gas, with sulphurous acid, and a dense fuming acid, being expelled, and metallic platina remaining. From this analysis Mr Davy inferred, that the oxide which is its base, the black oxide as he named it, consists of 89.1 of platina, and 10.9 of oxygen, and that it consists of 73.7 of oxide, and 26.3 of sulphuric acid *.

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* Philosophical Magazine, vol. xl. p. 354.

Vauquelin has lately stated, that if the insoluble muriate of platina be boiled with sulphuric acid nearly to dryness, muriatic acid is discharged, and a black mass remains, which is soluble in water, and does not precipitate a solution of silver, if sufficient time has been employed in the operation, and enough of sulphuric acid used. It is a true sulphate; it is deliquescent, and appears not susceptible of crystallizing; its solution is of a yellowish green colour. The alkalis at first only deepen its colour, but after some days a bulky precipitate is thrown down; this washed with water and dried, is of a brilliant black colour; it loses sixteen hundredths of its weight by heat, and is reduced to the metallic state. With sulphate of potash it forms an insoluble triple compound.

Mr E. Davy found, that triple sulphates can be formed from the binary sulphate, by the addition of the alkalis and earths, analogous to the triple muriates of platina. The Potassa-sulphate of platina is formed by neutralizing an aqueous solution of sulphate of platina by a solution of potash, and boiling for a short time. It is in small grains of a black colour, with considerable lustre; is tasteless, and insoluble in water. It dissolves in muriatic acid, and forms muriate of platina and muriate of potash; but is little affected by the other acids, or even by the nitro-muriatic. It is decomposed by exposure to a red heat, affording water, oxygen gas, metallic platina, and sulphate of potash; its composition was hence inferred to be, 74 of platina, 9 of oxygen, 11.5 of dry sulphate of potash, and 5.5 of water. The Soda-sulphate of Platina is formed in a similar manner by the action of soda, and in its properties is very similar to the other; it was inferred to consist of 82.46 of oxide of platina, 8.66 of sulphate of soda, and 8.88 of water. The Ammoniaco-sulphate of platina has a similar resemblance of properties to the others; its composition was inferred to be 70 of oxide of platina, and 30 of sulphate of ammonia and water. The Alumina-sulphate, and Baryta-sulphate, have the same general characters *.

Mr E. Davy discovered, that by the medium of sulphate of platina a fulminating preparation may be obtained, analogous to fulminating gold. The watery solution of the sulphate is treated with a slight excess of ammonia; the precipitate is placed on a filtre, and partially dried; this ammoniaco-sulphate is boiled in a strong solution of potash nearly to dryness, a quantity of water is added, the whole is thrown on a filtre, and the solid matter, after being well washed, is dried at a temperature of about 212°. It forms a loosely coherent brown powder; when heated to 410° or 420°, it explodes with a loud report; and a minute quantity, such as a grain, occasions indentation in a copper plate; it explodes feebly from friction, and not at all from percussion. In its explosion by heat it affords nitrogen gas, ammonia, water, and metallic platina. Mr Davy inferred, that it is composed of 82.5 of oxide of platina, 9 of ammonia, and 8.5 of water †.

Platina, exposed to heat with sulphur under exposure to the atmosphere, forms no combination with it; but it occurred to Mr E. Davy, that if they were heated in a close tube, so as to prevent the volatilization of the sulphur, or if the ammoniaco-muriate of platina and sulphur were heated, so as to allow the saline matter to be volatilized, the combination might be effected. He accordingly found both methods to be successful. He has described two compounds. One, the super-sulphuret, is formed by heating, in a glass retort over mercury, a mixture of the ammoniaco-muriate of platina, with two-thirds of its weight of sulphur. It is in powder, or in small masses of a dark grey colour, having a specific gravity of 3.5; dull, or with

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* Philosophical Magazine, vol. xl. p. 350.

† Philosophical Transactions, 1818, p. 136.

a feeble metallic lustre; soft; not affected by the acids, nor by water or atmospheric air; not capable of being fused; nor decomposed by a red heat if the air is excluded, but in the atmosphere undergoing entire decomposition. From its analysis in this mode he found it to consist of 72 of platina, and 28 of sulphur. A sub-sulphuret is formed by heating platina with sulphur in an exhausted tube; it is dull and earthy, having a specific gravity about 6.2; of a bluish grey colour, and in its chemical properties resembles the other: it consists of 84 of platina, and 16 of sulphur *. Vauquelin has more lately formed a compound by similar processes, to which he assigns precisely the same proportions. He describes it, when formed by the medium of the ammoniaco-muriate, as in the form of brilliant needles of a black colour. In passing a current of sulphuretted hydrogen through a solution of muriate of platina, a precipitate is formed of a deep black colour, which, after being dried, lost 23 of weight from 100 by calcination, and might therefore be supposed to be a super-sulphuret; but this loss he found to be partly from the escape of water and sulphurous acid; the precipitate, therefore, appeared to be a hydro-sulphuretted oxide †. Mr E. Davy had, in some previous experiments, considered it as a sulphuretted hydro-sulphuret, or as a compound of platina, sulphur, and sulphuretted hydrogen. A distinguishing property of it, first observed by Proust, is that of forming sulphuric acid while drying in the atmosphere, so that it burns paper on which it is laid, an effect probably owing to the dense state in which the hydrogen exists in it, and the weak affinity by which it is retained facilitating the absorption of oxygen. The alkaline sulphurets appear to combine with platina by fusion; and they throw down a dark coloured precipitate from its solutions.

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* Philosophical Magazine, vol. xl. p. 27.

† Annales de Chimie et Physique, tom. v. p. 260.

Pelletier found, that platina may be combined with phosphorus, either by projecting small pieces of phosphorus on the platina, raised to a red heat in a crucible, or by exposing to heat a mixture of equal parts of platina and concrete phosphoric acid, with the addition of one-eighth of the weight of the mixture of charcoal powder. The phosphuret of platina is of a silvery white colour, very brittle, and so hard as to give sparks with steel: it is much more fusible than the metal: exposed to a strong fire, the phosphorus is expelled; and in this way Pelletier endeavoured to obtain platina in a convenient form. Mr E. Davy produced this combination of platina and phosphorus by the same methods as those which were successful with sulphur, and has described two compounds as the products, analogous to the sulphurets. The super-phosphuret is in powder, or in small pieces having a dull metallic lustre, of a black colour, of a specific gravity about 5.3; it is not affected by exposure to air or water; and is little affected by the mineral acids: it fuses at a white heat. Its composition, determined by synthesis, is that of 70 of platina, and 30 of phosphorus. The sub-phosphuret is formed by heating platina and phosphorus in an exhausted tube; they combine with vivid ignition; it is of a bluish grey colour, in small masses, or crystallized in small cubes; when it has undergone perfect fusion, its lustre is metallic; its chemical properties are analogous to those of the super-phosphuret: it consists, according to synthetic experiments, of platina 82.5, and phosphorus 17.5. Phosphuretted hydrogen transmitted through a solution of muriate of platina, causes the formation of a precipitate which appears to be similar to the sub-phosphuret*.

Platina unites with the greater number of the metals. These combinations, however, would require to be again submitted to examination, as they have not hitherto been

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* Philosophical Magazine, vol. xl. p. 52. 264.

obtained from pure platina. In the experiments of Mr Hatchet, platina, purified by precipitation by muriate of ammonia, was added to gold, in the proportion of about one-fifteenth of the gold, and they were combined by fusion: the metal was of a yellowish white colour, like tarnished silver, highly ductile, and also elastic, so much so, that Mr Hatchet supposed it might be advantageously employed for the springs of watches, &c. Its specific gravity was 19.013; that of the platina in its loose state having been 18.717. Platina, it has been supposed, might be employed to adulterate gold; but the adulteration could not be practised to any extent, from the platina debasing so much the colour of the gold. From an experiment by Guyton *, it appears, that when the alloy does not contain more than 0.155 of platina, the alteration of colour is such, that it does not even present that of gold of the palest colour; and it is easily discovered by chemical tests, particularly by the precipitation of the platina by muriate of ammonia. The alloy with silver is of a dull colour, and is harder than pure silver. It is singular that the platina, in combination with gold and silver, becomes soluble in nitric acid †. With quicksilver platina was supposed not to combine; and in its dense state, the combination is not easily effected. Guyton has shewn, however, that a plate of platina is rendered brittle, and increases in weight, by being kept immersed in boiling quicksilver ‡; and the process of Moussin Poushkin to obtain pure platina, already given, proves, that when the platina is in that loose spongy state in which it is obtained when its precipitates are reduced by heat, it may be amalgamated without difficulty.

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* Annales de Chimie, tom. xlvii. p. 301.

† Ibid. tom. lxxxix. p. 148. Philosophical Magazine, vol. xl. p. 1.

‡ Annales de Chimie, tom. xxv. p. 12.

Platina derives value from its great hardness and infusibility, and from not being liable to be affected by air, water, or the greater number of chemical agents. From these qualities, it is in particular adapted to the construction of chemical vessels, as crucibles, evaporating basons, &c. These have the disadvantage of being eroded by some chemical agents, as the fixed alkalis, and even some of the neutral salts, particularly the nitrates, but for many operations are extremely convenient. Vessels of platina have even been employed lately for the concentration of sulphuric acid by heat, on a large scale. Platina has been used, alloyed with a portion of copper and arsenic, in the construction of mirrors for reflecting telescopes; a purpose to which this alley is well adapted, from giving a single image, from being susceptible of a high polish, and from not tarnishing on exposure to the air. Guyton has employed platina, from its infusibility, in the construction of a pyrometer. From its property of expanding less by heat than the other metals, it was selected by the French philosophers for constructing the rules or scales employed to measure the base of the chain of triangles, from which they estimated an arc of the meridian in France, on which they founded their lineal measures. From the same property, it is better adapted than any other metal, for making the pendulum-spring of watches. Mr Scott, who has made this application of it, found that when a coil of it is placed on the surface of a flat piece of metal, making one end of the spring fast, and marking exactly the other extremity, no expansion is visible when heat is applied *.

It has been proposed to cover copper-vessels with platina. The method is, to reduce the precipitate, obtained by muriate of ammonia from its solution in nitro-muriatic acid; the spongy metallic matter is triturated in a heated

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* Nicholson's Journal, vol. xxii. p. 148.

mortar with five parts of quicksilver, by which an amalgam is formed: this is applied to the surface of the clean copper, and the quicksilver is volatilized by heat, which favours the adhesion of the platina to the copper *. Mr Stoddart has stated, that brass or steel may be covered with platina, by the same process as that employed in covering steel with gold, already described; adding sulphuric ether to the solution of platina, removing the etherial solution of the muriate of platina from the acid beneath, and dipping the polished steel or brass into it †.

Platina has been applied to porcelain-painting by Klaproth. Gold and silver had been the only metals applied to this use, being adapted to it from not being oxidated by heat, and from their density in consequence of which they cover the surface completely. Silver, however, is liable to tarnish, and hence is seldom used. Klaproth found, that platina has not this inconvenience, and might therefore be introduced to diversify the painting with gold. His method is to reduce, by a low red heat, the precipitate of platina from its solution by muriate of ammonia: it is obtained in the form of a soft powder, which is mixed with the flux used for porcelain gilding, and applied with a brush to the porcelain: it is then burnt in by the requisite heat under a muffle, and burnished. The colour is silver-white, inclining to steel-grey; and if the platina be mixed in various proportions with gold, numerous shades of colour are obtained ‡.

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* Nicholson's Journal, vol. ix. p. 303.

† Ibid. vol. xi. p. 283.

‡ Philosophical Magazine, vol. xvii. p. 156.

CHAP. IV.

IRIDIUM.

Of the foreign metals associated with platina, and the history of which may next be given, Iridium is that which appears to be present in the largest quantity, and which is obtained in the least indirect manner. It received this name from Mr Tennant, from the variety of colours it displays in its combinations.

It constitutes the principal part of the black powder deposited during the solution of crude platina in nitro-muriatic acid, though a portion of it, in consequence of the reciprocal action of the platina, is also dissolved, and communicates to the solution, and the salts it affords, a red colour. It may be obtained, therefore, either from the black powder, or from the red precipitate thrown down from the solution by muriate of ammonia. There are some varieties of native platina, in which it appears to exist in larger proportion than in others: in what has been named by Proust, Black Platina, it is present in considerable quantity [*]; and there are other varieties in which it is not contained.

Descostils obtained the oxide of this metal, and observed its effect in communicating a red colour to the salts of platina, but he did not examine its properties in the metallic state [†]. Fourcroy and Vauquelin procured it in that state, but not free from the combination with the other

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[*] Annales de Chimie, tom. xlix. p. 177. 202.

[†] Journal de Physique, tom. lvii. p. 368, &c.

metal, Osmium, which accompanies it *. Mr Tennant discovered both metals, and distinguished them from each other †. To these investigations we are indebted chiefly for a knowledge of its properties. Berzelius has endeavoured to determine its degrees of oxidation; and more lately Vauquelin resumed the subject, and has given some additional facts ‡.

Fourcroy and Vauquelin operated on the black powder, deposited during the solution of crude platina in nitro-muriatic acid. This substance heated before the blowpipe did not melt, but became white, acquiring a metallic lustre; fused with borax, it is reduced into white metallic scales. When melted with twice its weight of potash, it formed with water a solution of an orange yellow colour, which became of a reddish brown by the addition of nitric acid; was precipitated of a reddish brown by the solution of silver, and of a dull red by the solution of quicksilver. Vauquelin inferred from these facts, that it contained, with the new metal, a portion of chrome: of this Mr Tennant could not discover any trace; and the metallic oxide in combination with the alkali he regarded as the metal to which he gave the name of Osmium, and which, in the property of communicating vivid colours, resembles chrome. Vauquelin affirms, however, from subsequent experiments, that it contains, along with osmium, a portion of chrome, though less than had at first appeared, and apparently accidentally, in the state of chromate of iron ||.

The following is the process which Fourcroy and Vauquelin employed to procure the new metal. The powder deposited during the solution of the platina in nitro-mu-

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* Annales de Chimie, tom. xlix.

† Philosophical Transactions, 1804, p. 415.

‡ Annales de Chimie, tom. lxxxix. p. 150. translated; Annals of Philosophy, vol. vi.

|| Annales de Chimie, tom. xlix. p. 220. lxxxix. p. 157.

riatic acid, is exposed to heat with an equal weight of potash; it is then washed with water, when it forms a solution of an orange-yellow colour; on the quantity of matter undissolved by the alkali, and which assumes a green colour, muriatic acid is digested, and a solution is obtained of a deep green, which becomes red by boiling. These alternate actions of the acid and alkali are repeated until the whole is dissolved. The green colour of the muriatic solution appeared to Fourcroy and Vauquelin to depend on the presence of iron. The oxide and muriate of the new metal are of a blue colour, which mixed with the yellow muriate of iron produces the green; and accordingly they found, that in proportion as the alternate application of the acid and alkali were repeated, the green colour became weaker from the iron being removed, and at the end, the solution in the acid was of a pure and rich blue.

To separate the iron, the solutions in muriatic acid were mixed, and evaporated to dryness: the solid matter was re-dissolved in water, and the solution filtered and made to boil; it acquired a fine red colour. Plates of zinc were put into the liquor, and a little muriatic acid was added; in a short time it became green, and then blue, from the iron, in consequence of the action of the zinc, passing to the minimum of oxidation, while at the same time the other metal was precipitated; the liquid became turbid, and deposited flocculi of a black colour, and much lustre. This precipitate being allowed to subside, it was washed first with water, and then with a little muriatic acid, to carry off any iron that might adhere to it: in drying it with a gentle heat, it became white, and assumed a metallic lustre. Another process which these chemists found to succeed, was, to treat the dry matter obtained by the evaporation of the muriatic solutions with alkohol: this dissolved the whole of the muriate of iron; and the muriate of iridium remained under the form of a red powder, which might be decomposed by calcination in a silver or platina bason.

The process which Mr Tennant followed was similar. A quantity of the black powder was put into a silver crucible, with a large proportion of pure soda, and kept at a red heat: water being added, it formed a solution of a deep orange or brownish yellow colour, but much of the powder remained undissolved. This powder digested in muriatic acid, gave a dark blue solution, which became of a dusky olive green, and, by continuing the heat, a deep red colour. Part of the powder being yet undissolved by the acid, was heated as before with the alkali, and by the alternate action of the alkali and acid, the whole appeared to be capable of solution; a little silex, which appeared to have been chemically combined in the powder, being also taken up by the alkali. The alkaline solution contains the oxide of osmium: the acid solution contains both metals, but principally iridium. To obtain it, the liquor was submitted to slow evaporation, so as to form a crystallized mass. This, on being dried, and again dissolved in water, afforded by evaporation octaedral crystals; which, dissolved in water, gave a deep red coloured solution. Iridium may be obtained from these crystals, by exposing them to heat, which expels the oxygen and the muriatic acid: it appeared of a white colour, but was not capable of being melted by any degree of heat that could be applied.

Vauquelin has, in his last investigation of this subject, remarked, that nitrate of potash is preferable to the alkali in decomposing the black powder, as it promotes the oxidation of the osmium and chrome. The iridium procured in the acid solution may be rendered more pure than in the preceding processes, by taking advantage of a property belonging to it, that when in that state of oxidation in which it forms red solutions, it is only precipitated by muriate of ammonia, in the state of a triple compound. The muriatic solution, therefore, is to be boiled with nitric acid until this effect is obtained. The liquid is neutralized by ammonia; by boiling, any iron and titanium present are thrown down; the iridium may then be precipitated by muriate of ammonia, and the precipitate is decomposed at a red heat, so as to leave the metal in a state of purity.

Though Mr Tennant could not procure iridium in its proper state of aggregation, from its infusibility, it was obtained in this state by Descostils, and by Fourcroy and Vauquelin; though not altogether pure. They described it as of a greyish white colour, similar to that of platina; brittle, and easily pulverized. Mr Children procured it fused into an imperfect globule, by the intense heat of his powerful galvanic battery; he found it to be white, very brilliant, and of a specific gravity of 18.6, even in its porous state. Vauquelin has found too, that it is somewhat ductile. It appears to be capable of being volatilized by heat, as, when heated strongly before the blowpipe, it gives a white smoke, and disappears; and in fusing it with borax, it loses weight.

It is not difficult of oxidation. By applying a very strong heat to crude platina in an earthen retort, Descostils obtained a sublimate of a blue colour, which is oxide of iridium. And Fourcroy and Vauquelin remarked, that the matter, calcined with an equal quantity of potash, suffers oxidation from the atmospheric air, and forms with the alkali a green coloured mass. If this is diluted with water, the potash is dissolved, carrying with it a portion of the oxide, which communicates to it a red colour, or if the iridium is fully oxidated and pure, a blue colour; and in these combinations, the metal is susceptible of different degrees of oxidation, rendered evident by the different colours it assumes. But the degrees of oxidation have not been determined with any precision.

No unmixed acid attacks this metal: even the nitro-muriatic acid has a weak action upon it, and dissolves with the assistance of heat a very small portion: alloyed with platina, it is more soluble. It communicates to the acid a red colour, which, as the solution is evaporated, is changed to blue, the red re-appearing when the evaporation is carried to dryness.

The fixed alkalis exert a much more powerful action on it. When potash is heated with it, it causes its oxidation, and combines with its oxide. A mass is obtained of a black colour, which with water forms a solution of a deep blue colour. This seems to be the compound with excess of alkali; a portion which remains undissolved consists of the metal likewise oxidated with a smaller portion of alkali, as is shewn by its being soluble in muriatic acid, and affording by evaporation a triple muriate of iridium. Sometimes the alkaline solution is of a purple colour, from a portion of the compound of the metal, in that state of oxidation which gives the red colour, being dissolved alongst with that which gives the blue.

When the metal has been oxidated by the aid of an alkali and atmospheric air, it dissolves easily in the mineral acids: the sulphuric and muriatic acids become green or blue, according as they are more or less diluted with water: the nitric acid, when concentrated, forms a red solution. What is singular, the blue solutions become yellowish red when long boiled, and also become red when much diluted. Precipitates have been said to be thrown down from these solutions by the alkalis, of the same colour as the colour of the liquor; but, according to Vauquelin, the blue solutions are not precipitated by the alkali. The red muriatic solution forms with the alkalis triple compounds of sparing solubility.

When these solutions are free from iron, they suffer no alteration from prussiate of potash. The tincture of galls, aided by a small quantity of alkali, causes the liquor to assume a violet colour, and at length forms a reddish-brown precipitate. According to Mr Tennant, the solution of the crystallized muriate of iridium, of a deep red colour, is rendered colourless without forming any precipitate, by infusion of galls, prussiate of potash, muriate of tin, and carbonate of potash. Sulphate of iron, according to Vauquelin, renders the red solution of iridium at first violet, afterwards green, and at length nearly colourless. Sulphuretted hydrogen, and the hydro-sulphurets, destroy the colour of the solution, and, when heat is applied, precipitate a powder of a brownish-black colour. The greater number of the metals cause the red colour of the solution to disappear, and throw down a precipitate of a dark colour, according to Tennant; and according to Vauquelin, one consisting of green flocculi. Oxymuriatic acid in general restores the colour of those solutions which have been discoloured; giving to each its original colour, whether blue or red; but, according to Vauquelin, if after restoring the blue colour, a new quantity of oxymuriatic acid be added, that colour passes into a purple red; yet if the liquor in this state be left exposed to the air to allow the oxymuriatic acid to exhale, it resumes its blue colour. It can scarcely be doubted that these changes depend on the state of oxidation, and that this metal passes through different degrees of oxidation in these solutions with great facility. It may be inferred, too, that in the solutions of a red colour, it is more highly oxidated than in the blue, but this, as Vauquelin remarks, is not unequivocally determined.

Though the blue solutions of iridium are not precipitated by the alkalis when the metal is pure, precipitates are formed if iron, titanium, silica, or alumina, be present, from their affinity to oxide of iridium. The affinity to alumina appears to be strong, and the compound has an intense blue colour.

The salts of iridium have not been minutely examined. What have been obtained have been chiefly the triple alkaline muriates. The Potassa-muriate is formed when a solution of muriate of potash is mixed with a solution of iridium, or when, after exposing a mixture of iridium and potash to a red heat, the product is dissolved in water. It has a colour so intense as to appear black, but by spread-ing out is shewn to be purple. Though very little soluble in water, Vauquelin procured it in small octohedral crystals. It is decomposed by heat, and the metal remains with muriate of potash. The Ammoniaco-muriate is formed when ammonia is added to the red muriatic solution of iridium. Vauquelin states, that it is of a very deep purple colour; it is sparingly soluble in water, 20 parts of water being requisite for its solution at 60° ; the solution has an orange-red colour, intensely deep considering the quantity of salt dissolved, so that it imparts colour to a very large quantity of water. Ammonia discolours the solution without causing any precipitation ; and sulphate of iron, or metallic sulphurets, render it colourless ; oxymuriatic acid added restores the colour. This salt is decomposed by heat, giving out nitrogen gas, muriatic acid, and muriate of ammonia, and leaving metallic iridium in the proportion of 45 from 100 of the dry salt. Muriate of iridium may be obtained pure by passing oxymuriatic gas in sufficient quantity over the ammoniaco-muriate; the ammonia is decomposed ; and the pure muriate at length remains of a yellowish red colour.

Iridium, Mr Tennant found, does not combine directly with sulphur, but if the ammoniaco-muriate be mixed with an equal weight of sulphur, and be heated to redness, the sulphuret, according to Vauquelin, is formed. It is a black agglutinated powder.

Mr Tennant combined this metal with some of the other metals. It did not unite with arsenic. Lead combines with it easily, but is separated by cupellation. Copper forms with it a malleable alloy, much harder, according to Vauquelin, than pure copper, and of a pale colour: with tin it gives a dull white alloy hard and malleable ; silver may be combined with it, and remains malleable, nor is the iridium separated from it by cupellation ; it appeared, however, to be not perfectly combined with the silver, but rather diffused through its substance in the state of a powder.

Gold alloyed with it is malleable, nor is the colour much different from that of pure gold. The iridium is not separated by cupellation: from the alloy, both of silver and gold, it is separated by solution, remaining in the form of a black powder, while these metals are dissolved.

CHAP. V.

OSMIUM.

In the account of Iridium it has been stated, that when the black powder deposited during the solution of crude platina in nitro-muriatic acid is fused with soda or potash, while part of it remains undissolved, a portion enters into combination with the alkali, forming a compound soluble in water. This matter, dissolved by the soda, was examined by Mr Tennant, and considered by him as the oxide of a new metal, which, from a peculiar property belonging to it, of its oxide having a strong smell, he named Osmium *. Some of its properties were observed by Fourcroy and Vauquelin, in their examination of iridium †, particularly the acrimony of the vapour of its oxide, and its staining the skin, and giving a blue colour on the addition of infusion of galls to its solution; but they did not recognize it as a distinct metal. Lately Vauquelin has added some important facts to its history ‡.

The oxide of osmium is not at once extracted from the black powder in the above process; the repeated and alternate applications of soda or potash, and of muriatic acid, are required; the acid dissolving principally the iridium, the

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* Philosophical Transactions, 1804.

† Annales de Chimie, tom. l. p. 9. 14. 25. ‡ Ibid. tom. lxxxix.

alkali the osmium. The oxide of osmium is detached from its combination with the alkali by any acid, and, what is a singular property, may be obtained in solution in water by distillation. The sulphuric acid not being volatile, answers best for this purpose, though, as even a little of it is liable to pass over, a second slow distillation is required to obtain the oxide perfectly free from it. The solution thus obtained is without colour, has a sweetish taste, and a very pungent and peculiar smell. Paper stained blue with violets is not reddened by it, but, exposed to the vapour arising from it in a phial, it loses much of its blue colour, and inclines to grey. Laugier has stated, that the acid employed in the solution of the platina, contains a considerable quantity of oxide of osmium, which may be obtained by first distilling the acid from the platina, and then saturating the distilled acid with an alkali or lime, and distilling it a second time *.

Another mode by which oxide of osmium is obtained, is, to distil with nitre the black powder procured from platina, with a degree of heat hardly red: there sublimes into the neck of the retort a fluid apparently oily, which on cooling concretes into a solid, colourless, semi-transparent mass, soluble in water. The oxide in this concentrated state, stains the skin of a dark colour, which cannot be effaced.

To reduce the oxide to the metallic form, Mr Tennant employed the action of another metal. By agitation of the solution of the oxide in water with quicksilver, it loses its smell, and the metal combining with the quicksilver forms an amalgam. From this much of the mercury may be separated by pressure through leather; the remaining amalgam being exposed to heat, the mercury is distilled off, and a powder is left of a dark grey colour, which is osmium. By exposing it to heat with access of air, it is ox-

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* Annales de Chimie, tom. lxxxix. p. 191.

idated, and evaporates with the usual smell; but if this is prevented, the metal does not appear volatile or fusible. Being subjected to a strong white heat in a cavity in charcoal, it was not melted, nor did it undergo any apparent alteration. When exposed to heat in a similar situation with copper and with gold, it melted with each of them, forming alloys which were quite malleable, and which, dissolved in nitro-muriatic acid, afforded by distillation oxide of osmium.

It is obvious, that in this process the metallic state was only imperfectly obtained; nor has it been procured in any other state than that of a powder; its difficult fusibility, its facility of oxidating, and the volatility of its oxide, preventing its assuming the usual physical properties of a metal. As the oxide on being precipitated from its solution by zinc, assumes a deep blue, Vauquelin supposes this to be the colour of the metal; but the blue powder may be a suboxide. When heated and rubbed against a hard polished body, it exhibits a copper red surface.

When the reduced osmium is heated in the air, it is volatilized, but it is at the same time oxidated, as is apparent from the pungency of the vapour.

When it is heated in a retort luted, Vauquelin found, that before the bottom was raised to a red heat, brilliant white crystals were condensed in the neck; afterwards, as the heat increased, a blue crust was formed on the upper part. The first of these is pure oxide of osmium, the production of which ceases, from the oxygen of the air in the retort being exhausted. Its production, however, commences at so low a temperature, that he supposed it probable that it is not formed entirely by the action of the air, but that the powder supposed to be metallic osmium retains a little oxygen, which, when it is heated, unites with a portion of the metal, and forms the volatile oxide; and this seems nearly established by the fact, that the powder which has afforded the oxide by volatilization, does not afford more at the same temperature, although air be admitted. The blue sublimate is probably a sub-oxide.

Vauquelin appears to have obtained the oxide of osmium by this process, in a purer state than that in which it was obtained by Mr Tennant. He describes it as being in white, transparent, and brilliant crystals; its taste is very strong and caustic; its odour is insupportable, especially when it is in the state of vapour. It is more fusible than wax, and has a similar tenacity; and it is very volatile. It blackens vegetable and animal substances, especially if moist, and it is extremely soluble in water.

The most striking test of oxide of osmium, is infusion of galls, which produces a purple colour in its solution, which soon becomes of a deep blue. It may thus be recognized, when contained even in the solution of iridium; the red colour of the latter first disappearing, on the addition of infusion of galls, and the purple and blue colour, from the action of the osmium, soon appearing. The solution of oxide of osmium becomes yellowish with pure ammonia, and with carbonate of soda; with potash and lime, compounds of a bright yellow colour are formed: by magnesia its solution is not affected.

Oxide of osmium appears to form combinations with the alkalis of considerable permanence. This is apparent from its volatilization being prevented by the action of the alkali in the mode of extracting it from native platina. The addition of an alkali too, to its solution, diminishes greatly the pungency of its odour.

Oxide of osmium is easily de-oxidated. It becomes of a black colour with alkohol or ether, and separates in the form of black films. It parts, too, with its oxygen to all the metals excepting gold and platina. Silver kept in a solution of it acquires a dark colour, but does not entirely deprive it of smell. Copper, tin, zinc, and phosphorus, produce a black powder, and deprive the solution of all smell, and of the power of turning galls of a blue colour:

this powder consists of the osmium in a metallic state, with the oxide of the metal employed to precipitate it.

Metallic osmium had been stated by Mr Tennant not to be acted on by any acid, not even the nitro-muriatic; and to be rendered soluble only by being previously heated with an alkali. According to Vauquelin, however, it dissolves in muriatic acid when assisted by heat, the solution being at first green, but soon becoming reddish-yellow. And if to the muriatic acid, a few drops of nitric acid are added, the solution takes place more readily. When oxymuriatic acid gas is brought into contact with it, it appears to melt, assumes a beautiful green colour, and is at length entirely dissolved, forming a small quantity of a brownish red liquid. A drop or two of this solution being diluted with water, infusion of galls produced a very deep blue colour. Potash gave a yellow colour. And zinc precipitated osmium. During these solutions, much oxide of osmium is volatilized. That osmium is not easily extracted from native platina by acids, Vauquelin supposes owing to its being protected by the action of iridium. From the observation of Laugier, however, already stated, it appears, that more is dissolved than had been noticed; and therefore, that it exists in native platina, in larger quantity than has been supposed.

The properties of this substance are on the whole extremely peculiar, and differ greatly from those of the metals in general.

CHAP. VI.

RHODIUM.

This metal was discovered along with palladium in native platina, by Dr Wollaston. He gave it the name of Rhodium from the rose colour of its salts and solutions. His experiments were confirmed by Descostils *. And more lately some facts with regard to it have been stated by Berzelius †, and by Vauquelin ‡.

Dr Wollaston remarked, that after the precipitation of the solution of platina in nitro-muriatic acid, by muriate of ammonia, certain metals still remain in solution. These are copper and lead, with rhodium and palladium. The following is the process he employed to separate them.

Crude platina having been exposed to a red heat to expel any mercury, was digested in a small quantity of dilute nitro-muriatic acid, to abstract any gold that might be mixed with it. It was then dissolved in nitro-muriatic acid, diluted for the purpose of leaving undissolved as much as possible of the shining powder, and the whole was suffered to remain in a sand-heat till completely saturated. A portion of it, corresponding to 1000 grains of crude platina, was precipitated by a solution of an ounce of muriate of ammonia in hot water. The greater part of the platina was thus thrown down. In the remaining liquid,

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* Journal de Physique, tom. lxi. p. 399.

† Annals of Philosophy, vol. iii. p. 253.

‡ Annales de Chimie, tom. lxxxviii. or Philosophical Magazine, vol. xliv. p. 53.

a piece of clean zinc was immersed, and allowed to remain until no farther action appeared to be exerted. The iron present remained in solution, the other metals were precipitated in the form of a black powder, estimated to amount to between 40 and 50 grains. This precipitate, which by previous experiment was known to consist of platina, rhodium, palladium, copper, and lead, was digested in very dilute nitric acid, by which the two latter metals were removed. The remainder was digested in nitro-muriatic acid; to the solution was added 20 grains of common salt; and the solid matter obtained by evaporation to dryness with a gentle heat, consisting of the triple salts of soda and muriatic acid, with oxides of platina, of palladium, and rhodium, was washed repeatedly with alkohol till it came off nearly colourless. The triple salt of rhodium remained undissolved. When dissolved in water, and decomposed by zinc, a black powder was obtained, in quantity corresponding to about 4 grains from the 1000 grains of crude platina dissolved. This powder, exposed to heat, continued black; with borax it acquired a white metallic lustre, but appeared infusible by any degree of heat. Like platina, it is rendered fusible by arsenic, as it also is by sulphur: the arsenic, or the sulphur, is expelled by a continuance of the heat; and the metallic matter obtained *. Vauquelin, in his memoir on rhodium, has stated some circumstances to be attended to in conducting this process, and has also given a different method by which it may be obtained. It is complicated, but the most essential circumstance is, that of separating the rhodium and palladium from their muriatic solution by adding ammonia, which precipitates the palladium in the state of a triple salt; the clear liquor is evaporated to dryness, and affords the pure ammoniaco-muriate of rhodium, which may then be reduced by heat.

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* Philosophical Transactions, 1804, p. 422.

Dr Wollaston was unable to bring the metallic matter of rhodium into fusion, or even to render it malleable. The specific gravity of the imperfectly agglutinated mass is about 11. Vauquelin remarks of it, that it appears to be the most infusible of all the metals; a stream of oxygen gas directed for a long time on ignited charcoal, on which it was placed, not fusing it completely: its colour he observed to be silvery white.

Berzelius has inferred the existence of three degrees of oxidation of this metal, in which 100 are combined with 6.71 of oxygen, with 13.42, and with 20.13. The prot-oxide is obtained by exposing the metal to a red heat in an open vessel; it gradually forms a black oxide, which, when rubbed, has no metallic brilliancy, and when heated with carbonaceous matter, is reduced with detonation: it is insoluble in acids. The deut-oxide is obtained by calcining powder of rhodium, with caustic potash and a little nitre; it remains in combination with the potash of a light brown colour, and may be separated by an acid, which unites with the alkali without dissolving the oxide. The per-oxide is obtained by precipitating the soda-muriate by potash; a reddish precipitate is thrown down, which is the hydrated oxide; when heated it gives off water, becomes of a darker colour, and at a heat below redness takes fire, gives out part of its oxygen, and is reduced to the state of prot-oxide.

This metal is altogether insoluble in acids. Even nitro-muriatic acid does not dissolve it; its being extracted therefore, from native platina by this acid, must be ascribed to the action of the metals accompanying it. Its oxide precipitated from the soda-muriate solution by an alkali, Dr Wollaston found to be soluble in every acid that he tried: its solution in muriatic acid did not crystallize on evaporation; the residuum was soluble in alkohol, and of a rose colour. Muriate of ammonia, or of soda, or nitrate of potash, occasioned no precipitate in it, but formed triple salts, which were not soluble in alkohol. The solution of it in nitric acid did not crystallize; but the metal was precipitated from it by silver, copper, and other metals.

The soda-muriate of rhodium is of a deep red colour; it is very soluble in water, and can be obtained in rhomboidal crystals. The ammoniaco-muriate obtained by evaporation from the muriatic solution, to which ammonia has been added, can be obtained in brilliant crystalline grains, or according to Laugier, in regular four-sided prisms of a deep garnet colour: its solution is of a purple red, which becomes brown when heated.

The solution of the triple salt of muriatic acid soda and oxide of rhodium, exhibits the following phenomena, when submitted to the common re-agents. Muriate of ammonia occasions no precipitation from it, but when a solution of platina is added, a precipitate is formed of a yellow colour. Prussiate of potash occasions no precipitation, neither does hydro-sulphuret of ammonia. Even carbonate of potash, of soda, or of ammonia, does not precipitate it; but the pure alkalis throw down a yellow oxide, which is dissolved by an excess of alkali.

Vauquelin formed sulphuret of rhodium by heating the ammoniaco-muriate with sulphur. A well-fused mass was obtained of a bluish white colour, which he inferred contains 26 per cent. of sulphur. When heated in contact with the air, it exhales sulphurous acid, and a white spongy brittle mass remains.

Rhodium unites with all metals that have been tried, except mercury. With gold or silver it forms very malleable alloys, which are not oxidated by a high degree of heat, but become encrusted with a black oxide when very slowly cooled. The colour of gold is so little altered, that even when the proportion of rhodium amounts to one-sixth, it is not different from that of fine gold. The alloy is less fusible than gold. In dissolving either the alloy of gold or silver, the rhodium remained untouched, either by nitric or nitro-muriatic acid. When one part of rhodium was fused with three parts of bismuth, of copper, or of lead, each of these alloys could be dissolved in a mixture of two parts, by measure, of muriatic with one part of nitric acid; and the muriate of rhodium had the same colour and properties as when pure.

CHAP. VII.

PALLADIUM.

THIS is the last of the new metals from native platina which we have to describe. It was discovered by Dr Wollaston, who, from the fanciful coincidence of the planet to which the name of Pallas was given having been discovered about the same time, gave it the name of Palladium. He has since found it native, nearly pure, in small fragments intermixed with native platina from Brazil *, and Mr Cloud has discovered it combined with gold from Brazil †. Some facts with regard to it have been added by Vauquelin ‡.

It is obtained from crude platina by the process already described for procuring rhodium; the triple salts of muriatic acid, and soda, with rhodium, palladium, and platina, remaining in the last stage of that process, previous to the affusion of alkohol. The alkohol is employed to separate these salts, that of rhodium not being soluble in it, while that of palladium is dissolved, with the small portion of muriate of soda and platina which is present. This

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* Philosophical Transactions, 1809, p. 189.

† Transactions of the American Philosophical Society, vol. vi.

‡ Annales de Chimie, tom. lxxxviii. or Philosophical Magazine, vol. xliv.

platina is precipitated from the solution by the addition of muriate of ammonia. To the solution, diluted prussiate of potash is added, which instantly occasions a precipitate of a deep orange colour at first, but afterwards changing to a green. This precipitate dried and heated, leaves a metallic residuum, amounting to about seven grains from the solution of 1000 grains of crude platina. When heated with borax, it communicates a dark brown colour to it, and acquires a bright metallic lustre, but does not fuse before the blowpipe: a little sulphur, however, causes it to melt immediately: from the globule thus obtained, the sulphur is expelled by exposure to the extremity of the flame of the blowpipe, and the palladium remains spongy and malleable *.

Several other processes have since been given by Dr Wollaston to obtain palladium. One of the simplest is, to add to a solution of crude platina, a solution of prussiate of mercury: the liquor becomes slightly turbid, and a flocculent precipitate is formed of a yellowish white colour. This consists wholly of prussiate of palladium, and, when heated, yields that metal in a pure state, amounting to about four or five tenths in the hundred, on the quantity of ore dissolved †. The process of Vauquelin to separate palladium from rhodium, has been noticed under the history of that metal.

Palladium is of a greyish white colour, similar to that of platina: it has, when polished, considerable lustre: it is ductile and very malleable; so that by the flatting-mill it can be reduced into thin slips, which are flexible, but not very elastic. Its fracture is fibrous, and shews a kind of crystalline arrangement. In hardness it is superior to forged iron. Its specific gravity varies, according to its perfect fusion, from 10.9 to 11.8. Like platina it is a less

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* Philosophical Transactions, 1804, p. 426.

† Ibid. 1805, p. 327.

perfect conductor of caloric than the other metals; and is also less expansible, though it is rather more so than that metal.

When exposed to a strong heat, its surface tarnishes, and becomes blue, but, by increasing the heat, it again becomes bright. At a heat above the melting point of gold, there is no appearance of fusion, but, by increasing the heat considerably, its fusion is accomplished. Vauquelin states, that it does not melt completely in the heat of a furnace, and it melts even imperfectly on ignited charcoal, excited by oxygen gas. The facility of its agglutination, when it is reduced from the muriate, is owing to the saline matter acting as a flux. When it is brought into fusion by oxygen gas, he remarked that it volatilizes, and also burns in brilliant sparks. Its oxides precipitated from its saline compounds, are reduced by heat to the metallic state.

Berzelius endeavoured to determine the proportion of oxygen with which palladium combines, by finding how much quicksilver is necessary to decompose a given quantity of its muriate, and then inferring the equivalent proportions. He found reason to admit the existence of one oxide only, composed of 87.56 of palladium, with 12.44 of oxygen, or 100 with 14.21 *.

It is acted on by a number of the acids. Nitric acid acquires from it a beautiful red colour, but the quantity dissolved is extremely small. The action of nitrous acid on it is more powerful. Sulphuric acid boiled on it, acquires the same red colour, and dissolves a small portion of it. The action of muriatic acid is similar. Nitro-muriatic acid forms with it a deep red solution. These solutions are decomposed by the alkalis and earths; precipitates being thrown down, generally of a beautiful orange colour: they are partly re-dissolved if the alkali be added in excess. The sulphate, nitrate, and muriate of potash

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* Annals of Philosophy, vol. v. p. 19.

or ammonia, produce, as Chenevix observed, a precipitate in the salts of palladium of an orange colour, as well as in those of platina, when they are not in too dilute a solution: according to the observation of Dr Wollaston, the solution requires to be concentrated; the salts form ternary compounds with oxide of palladium, which are very soluble. These precipitates are triple salts, and are all more soluble than the triple salts of platina. They are insoluble in alkohol. According to Vauquelin, the neutral muriate of palladium is not very soluble in water, but becomes abundantly soluble with an excess of acid. If muriate of ammonia be added to this solution, crystals in prisms are formed of a yellowish green colour. If ammonia is added to this salt, so as to saturate the excess of acid, another is formed, which is the ammoniaco-submuriate. It is obtained in the form of crystalline needles of a beautiful red colour, when at the *minimum* of acid; it is scarcely soluble in water, and communicates to it only a slight yellowish tinge; it is soluble in diluted muriatic acid, forming a solution of a yellowish brown colour. Ammonia added to this solution, again precipitates the salt red. When this salt is decomposed by the heat of a forge, it affords 40 *per cent.* of metallic palladium. Potash added to the muriatic solution, does not, according to Vauquelin, form a triple muriate, but throws down the oxide, especially when aided by heat.

The alkalis act on palladium. Exposed to potash in fusion, it loses its brilliancy, and part of its weight, a portion being combined with the alkali. The action of soda is less powerful. Ammonia allowed to remain for some days on palladium, acquires a bluish tinge, and holds a small portion of oxide in solution. In these cases, the action of the alkali is promoted by the atmospheric air, which affords oxygen to the metal.

The solutions of palladium in the acids are decomposed by a number of the usual re-agents. Recent muriate of tin, gives a dark orange or brown precipitate from the neutralized solutions; or if mixed in such proportion as to remain transparent, changes it to a beautiful emerald green. Green sulphate of iron throws down the palladium in a metallic state. A solution of sulphuretted hydrogen throw down a precipitate of a dark brown colour. Prussiate of potash causes an olive coloured precipitate; prussiate of mercury, a precipitate of a yellowish white colour; and as it does not precipitate platina, this is an excellent test of palladium. Dr Wollaston observed, that the precipitate by prussiate of mercury, from the neutral nitrous solution of palladium, detonates, when heated to 500° of Fahrenheit, with a noise similar to that of gunpowder. Infusion of galls, according to Vauquelin, produces no change in the solution of palladium. Fluoric, arsenic, phosphoric, oxalic, tartaric, citric, and some other acids, together with their salts, precipitate some of the solutions of palladium.

All the metals, with the exception of gold, silver, and platina, precipitate palladium from its solution in the metallic state.

Palladium combines readily with sulphur. If raised to a high heat, though not such as is sufficient to melt it, on throwing upon it a little sulphur, it is fused, and remains in fusion even at a low red heat: the sulphuret may also be formed by heating the ammoniaco-muriate with sulphur. 100 of palladium, according to Vauquelin, combine with 24 of sulphur. It is whiter than the metal, and is extremely brittle. By a strong heat the sulphur is dissipated, and the metal remains of a silver-white colour, and malleable.

Mr Chenevix did not find that palladium suffered any change of properties from being kept in fusion in a charcoal crucible. It appears therefore to form no combination with carbon.

He found that it could be alloyed with a number of the metals. With gold it forms an alloy of a grey colour, harder than gold, but less ductile than the palladium. Its fracture is coarse grained, and its specific gravity 11.079. Alloyed with an equal weight of silver, it gives a compound of a similar colour, hard, and having a specific gravity of 11.290. Equal parts of platina and palladium entered into fusion at a heat not much superior to that capable of fusing palladium alone. The alloy resembled the preceding in colour and hardness; its specific gravity was 15.141. The alloy of palladium, with an equal weight of copper, was more of a yellow colour, and hard and brittle. Lead was found to increase the fusibility of palladium, forming an alloy superior to all the former in hardness, but extremely brittle. Its specific gravity was 12.000. With iron, tin, bismuth, and arsenic, it forms alloys hard, and all of them brittle.

This metal having, when first announced, been offered for sale in small quantities, without any thing being made public as to its origin, and with an imperfect statement of its properties, Mr Chenevix suspected that it might be an alloy; and the striking similarity of many of its precipitates with those of platina, led him to suppose that it contained this metal. From the results of experiments which this led him to undertake *, he concluded, that it is an alloy of platina and quicksilver; and he supposed it to be formed by the process of precipitating a mixed solution of mercury and platina by green sulphate of iron, and exposing the precipitate to heat. He, however, found the success of the experiment to be very precarious; it has not succeeded with others; nor has any subsequent result confirmed the opinion. What indications of palladium were obtained, no doubt arose from the presence of palladium in the platina operated on; and the properties of this metal are so characteristic, as to lead to the belief that it is essentially distinct.

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* Philosophical Transactions, 1803, p. 290. 1805, p. 104.

CHAP. VIII.

QUICKSILVER OR MERCURY.

THIS metal is distinguished by its fluidity at any common natural temperature: at 40° or 39° below the zero of Fahrenheit's scale, it passes to the solid state. It forms the connection between the preceding metals and those the history of which is to follow. Like the latter, it can be oxidated by heating it in contact with atmospheric air; like the former, its oxides are reduced by exposure to heat alone, the oxygen being expelled, and the quicksilver returning to the metallic state. Though fluid, it is perfectly opaque, and is possessed of considerable lustre. It exists in nature, native, and more abundantly mineralized by sulphur; from this ore it is obtained by distillation, lime or iron being added to retain the sulphur. In the state in which it is usually sold, it is somewhat impure; at least, by mixing it with an equal weight of iron-filings, and distilling from an iron retort, it is obtained more bright and mobile. The nature of the action of the iron in this experiment is not very obvious: it is found, however, to be essential, and it has been supposed to operate by the affinity it may exert to the small portion of alloy, or of carbonaceous matter, which may be contained in common quicksilver.

Quicksilver, though liquid at any usual natural temperature, can, by a sufficient reduction of temperature, be obtained in the solid state. This was effected in 1759, by Professor Braun of Petersburgh: while occupied in experiments on the power of freezing mixtures, he found that the quicksilver in the thermometers which he employed was congealed, by immersion in a mixture of diluted nitric acid and snow. The congelation of quicksilver had also been frequently produced by the operation of natural cold, particularly in Siberia; Gmelin and others having observed the mercury in the thermometer to sink so low in the tube, as it could only have done in consequence of its congelation. Yet so general was the opinion of its natural fluidity, previous to Braun's experiments, that the just conclusion was not drawn *. From our knowledge of the modes of producing artificial cold, the experiment can now be easily performed.

In passing to the solid state, this metal suffers a remarkable condensation, equal, as Mr Cavendish inferred from the experiments of Braun and Hutchins, to its expansion, from an augmentation of temperature of 500° of Fahrenheit, which amounts to $\frac{1}{23}$ of its volume. This gave rise at one time to a very erroneous estimate of its freezing point. In Braun's experiments, the mercurial thermometers he employed sunk to—350° of Fahrenheit's scale, and, in subsequent experiments, even to—544° and—556°; below which it was concluded that the freezing point of quicksilver must be placed. But this is a deception, from the great contraction of the quicksilver at and previous to its congealing; by experiments made, so as to avoid this source of error, by Mr Hutchins at Hudson's Bay, its freezing point is fixed at—39° of Fahrenheit †.

In its liquid state, the specific gravity of quicksilver is, according to Brisson, 13.568: if the condensation which it suffers in becoming solid is equal to $\frac{1}{23}$, this gives its specific gravity, in the solid state, at its melting point, as equal to 14.176. Mr Biddle, by weighing congealed mercury, under alkohol, with the hydrostatic balance at

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* Philosophical Transactions, vol. lxxiii. p. 565.

† Ibid. p. 221.

—40, observing the loss of weight it sustained, and finding by a similar experiment, the loss of weight which an equal weight of silver, the specific gravity of which was known, sustained under the same circumstances, inferred that its specific gravity, at its melting point, is 15.612 *. The condensation appears, from this, to be greater than in the calculation of Mr Cavendish. Mr Biddle, however, on repeating the experiment, found, that the specific gravity of solid mercury is not so great as he had at first inferred. He states it at a little below the point of congelation, 14.465 †.

In congealing, quicksilver gives out a portion of caloric equal to what would raise its temperature while in the fluid form 152° of Fahrenheit ‡.

In its solid state, this metal possesses an evident degree of malleability, as it can be flattened with a hammer; at Hudson's Bay, it has been beaten on an anvil to the thinness of paper. It is not possible to estimate its ductility. Its hardness, when thus near to its melting point, does not appear to be considerable.

In congealing, it assumes a crystalline structure and form. In its structure, it presents the appearance of striæ diverging from different centres; and when the liquid part is withdrawn from a quantity partially congealed, small octaedral crystals are discoverable ||.

This metal is also easily volatilized: Dr Irvine found, with a mercurial thermometer, accurately graduated, that it boils at 672° §. Mr Crichton has stated it at 655° ¶:

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* Nicholson's Journal, vol. x. p. 253.

† Philosophical Magazine, vol. xxx. p. 145.

‡ Journal de l'Ecole Polytech. tom. i. p. 125.

|| Annales de Chimie, tom. xxix. p. 248.

§ Chemical Essays, p. 52.

¶ Philosophical Magazine, vol. xv. p. 147.

and Mr Dalton at 660°. It passes slowly into vapour at much lower temperatures.

At the same temperature nearly as that at which it is volatilized, quicksilver combines with oxygen. When heated in contact with atmospheric air, its lustre diminishes, a film forms on its surface, a powder of a dark red colour accumulates, and the oxygen of the air is absorbed. The production of this red oxide is difficult, as the attraction of the metal to oxygen is not strong; and by the requisite heat, a part of the quicksilver is volatilized. The apparatus which answers best, is a glass matrass with a wide bottom and long neck, the extremity of which is drawn into a small aperture, as this admits of the renewal of the atmospheric air, and the circulation of the mercurial vapour, without allowing much of it to escape. The heat is applied by the medium of sand, and it requires its application for a number of days, to oxidate any considerable portion of the metal. The oxide is in scales of a red colour. If exposed to the heat of ignition in a glass retort, it is decomposed, affording very pure oxygen, and returning to the state of quicksilver. This oxide exists in a number of the saline combinations of mercury; it is in particular the base of the corrosive muriate, and may be obtained from that compound by the action of the fixed alkalis.

Mercury, there is reason to conclude, can likewise be oxidated at a low temperature, by agitation or friction. It was known to the older chemists, that by long continued agitation, a black powder is formed from it; and by separating this, and subjecting the remaining quicksilver to agitation, there is the same result. Boerhaave formed a quantity of it by inclosing quicksilver in a strong bottle, which was fixed to the arm of a wind-mill. This has been regarded as a mechanical division of the metal, especially as it was found, that by exposing this powder to heat, it is reduced to running mercury. It has also been believed to be a real oxidation; but there is some doubt with regard to this, Priestley having found, in some of his experiments, that the air in which the quicksilver is agitated is not sensibly injured; though he also states, that the black powder, on being heated, becomes of an orange colour, dissolves like oxide of mercury in muriatic acid, and when heated strongly in a phial with common air, the air after the experiment becomes rather better, that is, contains more oxygen than before *.

This oxidation, (if it is to be regarded as such), can be more easily effected when the continuity of the mercury is divided by the interposition of any viscous matter, its surface thus increased, and the friction facilitated. Accordingly, by rubbing it with mucilage, oil, syrup, or honey, or even with dry powders, as chalk, the globules of mercury disappear; and in this way, a number of mercurial preparations are formed, used in medicine, and more active than metallic mercury.

The same oxide, or at least an oxide of definite composition, at a lower degree of oxidation than the red, is procured from some of the saline compounds of mercury, and more particularly from the mild muriate, or calomel as it is called. If this be triturated or digested with a solution of potash, the muriatic acid is abstracted, and a dark grey powder is obtained, which chemists have considered as the prot-oxide. It has lately been affirmed by Guibourt, that there is an intermixture in it of globules of mercury †; but this is not well established. Proust had before remarked, that it is only uniform when newly produced, and that it speedily changes its state of oxidation by one portion yielding oxygen to the other, so that it becomes at length a mixture of red oxide and metallic quicksilver ‡.

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* Experiments on Air, vol. iii. p. 467.

† Annales de Chimie et Physique, tom. i. p. 422.

‡ Journal de Physique, tom. lxxxi. p. 244.

The proportions of oxygen in these oxides have been variously estimated. Lavoisier, from the quantity of oxygen gas obtained from the reduction of the red oxide by heat, inferred, that it contains 7 of oxygen in 100 parts. Fourcroy and Thenard considered the black as composed of 100 metal with 4 of oxygen, and the red of 100 with 8. Proust inferred, from the results of the decomposition of the grey oxide by heat, that it consists of 100 of quicksilver with 3.7 of oxygen; and from a similar decomposition of the red, that it consists of 100 with 8.7 *. Sefstrom stated them at 100 with 3.95, and 100 with 7.9. Dr Wollaston has taken those of 100 with 4, and with 8, which may probably be regarded as the nighest approximations. In some other estimates which have been made from some of the salts of mercury, such as those by Chenevix, the proportion of oxygen appears to be stated too high.

The greater number of the acids act on mercury, are either capable of oxidating and dissolving it, or of combining with its oxides. These combinations have been more examined than perhaps those of any other metal, from their extensive medicinal applications, and are therefore well known.

Sulphuric acid has little effect on quicksilver, except when concentrated and aided by a high temperature. When boiled on it the acid is decomposed, the metal attracts a portion of its oxygen, and sulphurous acid gas is disengaged, while the oxide combines with another portion of the acid. When boiled nearly to dryness, a saline mass is obtained, white and composed of minute prismatic crystals. This differs considerably according to the proportions of the ingredients, and the degree of heat that has been applied. If two parts of acid have been used to one of metal, and if the process be stopt before the mixture

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* Journal de Physique, tom. lxxxi.

becomes dry, the soft mass obtained tastes extremely sour and styptic, is very caustic, deliquescent, and soluble in water. It is the perfect oxide of mercury combined with an excess of sulphuric acid. If only 1½ part of sulphuric acid be used, and if the process is stopt as soon as the mercury is converted into a saline mass, the metal is less perfectly oxidated, and is combined with less acid. If it be washed with water, the excess of acid, retaining a portion of oxide in combination with it, is carried off, and there remains a compound no longer sour, which is less acrid, much less soluble in water, requiring not less than 500 parts of boiling water for its solution, and which, by evaporation of its solution, affords prismatic crystals. This is the neutral sulphate, or salt resulting from the saturation of the imperfect oxide of mercury with sulphuric acid. It is likewise formed by diluting the acid with an equal quantity of water previous to its action on the quicksilver, little sulphurous acid being then disengaged, and the metal being brought only to a low state of oxidation. According to Fourcroy, who examined with much attention the results of the action of sulphuric acid on mercury, it consists of 75 of mercury, 8 of oxygen, 12 of sulphuric acid, and 5 of water.

By continuing the application of heat to any of these compounds, more of the acid is decomposed, and the metal is completely oxidated, while the remaining acid is unable to saturate this oxide. If a quantity of water is poured on this mass, it decomposes the sulphate of mercury; the greater part of the acid is abstracted, holding a portion of oxide in solution, and there remains the greater part of the oxide, with a portion of acid, still combined with it. The neutral sulphate is thus, by the affinity of the water, divided into a super-sulphate and sub-sulphate. The latter is in the form of a powder, of a lively yellow colour, nearly insoluble in water: it is a preparation formerly known by the name of Turbith Mineral, now named in the Pharmacopœia, Yellow Sub-Sulphate of Mercury. Although this can be obtained from the neutral sulphate, yet, to prepare it economically, the application of the heat ought to be continued to the saline mass, obtained by the action of the sulphuric acid on the metal, until it is perfectly dry; as thus, there is less excess of acid, and on adding the water, less super-sulphate, and, of course, more sub-sulphate is formed. The water ought also to be poured on the mass boiling hot; as, at a high temperature, it abstracts more of the acid from the oxide, and thus forms a larger quantity of sub-sulphate, as well as communicates a livelier yellow colour. According to Fourcroy, this sub-sulphate consists of 76 of mercury, with 11 of oxygen, 10 of sulphuric acid, and three of water; but its various shades of colour prove that the proportions of its ingredients may vary. Another analysis has accordingly given the proportions of 84.7 of oxide of mercury, 15 sulphuric acid, with 0.3 of water *. This preparation being uncertain, and occasionally violent in its operation, has been nearly banished from medical practice.

Sulphate of mercury is decomposed by the fixed alkalis, and by lime, and a precipitate is thrown down, supposed to be an oxide, but probably a sub-sulphate, the colour of which varies from a grey or a pale yellow to a red. Ammonia causes a precipitate of a grey colour; the precipitate is not so abundant as that from the fixed alkalis, as the ammonia dissolves a part of it, forming a triple compound, which by evaporation of the liquor may be obtained in small crystals. According to Fourcroy, this ammoniaco-mercurial sulphate consists of 39 of mercury, 33 of ammonia, 18 of sulphuric acid, and 10 of water. All these compounds are decomposed by heat, which expels first the acid, and afterwards the oxygen of the oxide.

Nitric or nitrous acid acts rapidly on mercury in the

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* Philosophical Magazine, vol. xxiii. p. 58.

cold.* Nitric oxide gas and nitrous acid vapour are disengaged, the metal is oxidated, and combines with a portion of the acid. The nature of this action is different, according to the circumstances under which it takes place, and the knowledge of it is important from its relation to the pharmaceutical preparations of mercury.

If the nitric acid is diluted with an equal part of water, and if no heat is applied to accelerate its action on the mercury, little nitric oxide gas is disengaged; the metal is combined with the smallest quantity of oxygen; and this imperfect oxide, as it may be named, is combined with the nitric acid. The acid can thus dissolve nearly twice its weight of mercury. If, again, it is in larger proportion, less diluted, and especially if its action be promoted by heat, it is rapidly decomposed: a large quantity of nitric oxide gas is expelled: less of the metal is dissolved, but it is saturated with oxygen; and this perfect oxide combines with the remaining acid. These two compounds are both named Nitrate of Mercury in the new nomenclature; but it is evident that they differ in their composition,—the one containing the metal in its lowest state of oxidation, the other containing it saturated with oxygen. Both, when the solution is completed, crystallize; the crystals being a congeries of slender prisms, or octaedrons if formed more slowly. They are deliquescent, and soluble in water; if the solution be merely heated, they are again dissolved. The difference between them is therefore not very great with regard to properties, but is easily discovered by their relations to other chemical agents, particularly by the different precipitates they afford when decomposed by the alkalis.

It is to be remarked, however, that the mercury is not easily obtained in the highest state of oxidation, by causing even the concentrated acid to act on the metal. It is obtained with more certainty by dissolving the perfect oxide of mercury in nitric acid. A compound of this kind is thus obtained which may be crystallized. These solutions too, have in general an excess of acid. This excess renders the saline combination more soluble, more permanent, and susceptible of dilution with water without decomposition, and likewise more acrid and corrosive: it is the common state of solutions prepared in the cold.

On the other hand, a nitrate of mercury may be formed with an excess of oxide. This is obtained, either when nitric acid, diluted with an equal weight of water, is boiled on quicksilver, until it can dissolve no larger portion of the metal, or by adding to a solution of nitrate of mercury, prepared in the cold, a quantity of metallic mercury, and boiling them together, the heat in both cases aiding the decomposition of the acid, and the oxidation of a larger portion of the metal. This compound, though it has an excess of oxide, remains soluble, and as it cools crystallizes; but if water is added to it, it becomes turbid, and a sub-nitrate of mercury, sparingly soluble, is precipitated, while a portion of neutral nitrate remains in solution. This nitrate of mercury, with excess of oxide, appears either to contain the metal in two degrees of oxidation, forming separate compounds, or, what is more probable, in a state of oxidation intermediate between that of the two neutral nitrates above described, and capable of being easily subverted; for when muriatic acid is added, portions of the two definite compounds which result from the union of that acid, with mercury in two states of oxidation, are formed; the muriatic acid, by its affinity, resolving the medium oxide, as it may be named, of the nitrate, into these two oxides with which it unites. It appears difficult to form a sub-nitrate of mercury, in which the metal is entirely either at the *maximum* or *minimum* of oxidation.

If any of the nitrous solutions of mercury be reduced by evaporation to a dry mass, the metal passes to a high state of oxidation, by the temperature facilitating the decomposition of the acid; and, at the same time, more or less of the acid is disengaged, as the heat is raised. The mass thus acquires at first a yellow colour, and at length it assumes a brilliant red colour and scaly appearance. This is a preparation which has long been used in medicine as an escharotic, under the name of Red Precipitate of Mercury. The process for preparing it, is to dissolve quicksilver in rather more than its own weight of diluted nitric acid, with the assistance of heat; continuing the heat, until the solution is reduced, by evaporation, to a dry mass, which, being reduced to powder, is urged with a strong fire, until it assume the brilliant red colour. It is difficult, however, to give this brilliant redness. Many directions have been given to attain it, but the greater number are useless or prejudicial. Much appears to depend on the quantity in which it is prepared. According to M. Payssé, who had examined the process as carried on in some of the chemical manufactories in Holland on a large scale, and who has given a memoir on this subject *, it depends principally on the heat being equally and steadily applied, without being raised too strong, by which the bright red colour is destroyed; and he has given the following process for its preparation: " Take mercury, free from every other metallic matter, 50 parts; nitric acid, deprived as much as possible of muriatic acid, and of from 34 to 38 degrees, 70 parts; dissolve the metal in the acid, and assist their reciprocal action by a gentle heat in a sand-bath; evaporate by distillation, and take the receiver from the retort when the vapours of the nitrous gas begin to manifest themselves, as they announce the decomposition of the mercurial nitrate. The point here is to employ a constant and moderate temperature, if you wish to insure success to the operation: it is raised a little towards the end, that is to say, when the disengagement of the gaseous nitrous

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* Annales de Chimie, tom. li. p. 202.; or Philosophical Magazine, vol. xxii. p. 126.

acid is no longer manifested, but in a manner not very sensible: the vessel must be exposed to this degree of heat, till it is observed that the mass of red mercurial oxide is of a bright and brilliant red colour in all its parts. Eight hours of heat are in general sufficient for 400 pounds of this substance."

This preparation has been regarded as an oxide of mercury, the whole of the acid being supposed to be expelled from it by the heat: but it is more probable that a portion of the acid will be retained by the affinity of the oxide to it, aided by the relative quantity: the preparation, too, is different in its appearance from the red oxide of mercury, prepared by exposing mercury to the action of atmospheric air at a high temperature; and is always more acrid and corrosive,—qualities probably derived from the acid it contains. I have found, accordingly, that it contains nitric acid: when water has been boiled on it, a liquor is obtained by filtration, having a styptic metallic taste, and which gives a white precipitate with solution of ammonia, or of carbonate of potash, a sufficient proof that it holds nitrate of mercury dissolved. The proper name of the preparation is Red Sub-Nitrate of Mercury. M. Payssé has stated, that when decomposed by heat, 100 parts afford 82 of mercury, and 18 of oxygen, while the preparation, which is of a dull red colour, does not give more than 13 or 14 of oxygen in this decomposition.

Nitrate of mercury is decomposed by the alkalis, and by several of the earths. The phenomena of these decompositions are different, according to the oxidation of the metal. If potash, soda, or lime, is added to the solution of mercury made in the cold and with the diluted acid, in which it is little oxidated, a greyish precipitate, with a tinge of yellow, is produced: when added to the solution in which the metal is more highly oxidated, the precipitate is yellow, with a mixture of white. In both cases, the alkali combines with the acid, and separates the oxide. The difference, therefore, in the precipitate, shews the different states of oxidation in which the metal exists in these solutions. The precipitated oxide still retains a portion of the acid in combination, as Bayen proved. According to Proust, however, the precipitate from the solution in the high state of oxidation is the red oxide pure.

Ammonia exerts a more peculiar action on the nitrates of mercury, which requires to be particularly noticed.

If the solution of mercury be that which contains the metal in the least oxidated state, the precipitate is of a dark blue colour, approaching to black: it is the metal in the lowest state of oxidation; and as it is mild in its operation, it is often used in medicine. It is inserted in the Pharmacopœia under the name of Oxidum Hydrargyri Cinereum. To prepare it, four parts of quicksilver are dissolved in five parts of diluted nitrous acid, that is, of acid diluted with an equal weight of water, the solution is diluted with 15 parts of distilled water, and water of carbonate of ammonia is added as long as any precipitation is produced: the precipitate is then washed with water, and dried.

In this process, it was supposed that the ammonia merely combines with the nitric acid, and that the oxide of mercury is precipitated. The precipitate, however, is different from that produced by adding to the same solution the fixed alkalis or lime, either of which attracts the acid, and separates the oxide; hence it is evident, that the ammonia re-acts on the oxide which it separates, and produces in it some change. According to Fourcroy, part of the oxygen of the oxide is abstracted by the hydrogen of the ammonia, the corresponding nitrogen being disengaged. The metal is thus reduced to its lowest state of oxidation,—one lower than that in which it existed in the nitrate of mercury. Others have affirmed, that the peculiarity of this precipitate arises from a portion of ammonia having combined with the oxide; but when well washed it does not exhale any ammoniacal smell, when submitted to the action of substances by which ammonia if present would be expelled.

The action of ammonia now described, is that which it exerts upon the solution of mercury in nitric acid diluted and in the cold, in which the metal is only imperfectly oxidated. Its action is different upon the solution in which, from the use of a concentrated acid, or the application of heat, the metal is more highly oxidated. The precipitate thrown down is white. Fourcroy found that this is a ternary combination of oxide of mercury, ammonia, and nitric acid. When the ammonia is added to the solution, it combines with part of the nitric acid, and separates the oxide, which, in the moment of its separation, attracts a portion of ammonia and of nitric acid, and forms this triple compound. It is decomposed by heat, and affords ammonia, nitrogen gas, oxygen, and mercury. According to Fourcroy, it consists of 68.2 of oxide of mercury, 16 of ammonia, and 15.8 of nitric acid and water*. It combines with an excess of ammonia, and is thus rendered more soluble in water.

The knowledge of the different states of oxidation in which mercury exists in combination with nitric acid, and of the action of ammonia on these oxides, enables us to determine the circumstances necessary to the proper preparation of the Grey Precipitate of Mercury, which, from these circumstances not being attended to, is met with very variable in its qualities, being sometimes of a dark colour, sometimes of a light blue, and of all the shades intermediate between these. These differences arise from the manner in which the solution of mercury has been prepared. If the acid has not been much diluted, or if the temperature has been high, with an excess of acid, the mercury will be highly oxidated; in this case, on adding ammonia, a

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* Annales de Chimie, tom. iv.

light coloured precipitate is thrown down. The object to be attended to, to obtain the dark coloured precipitate pure, is to diminish the action of the acid on the metal, as much as is compatible with the solution going on, the mercury being thus less perfectly oxidated. A process of this kind has been described by Hahneman, which answers exceedingly well. The acid is diluted with two parts of water, only one-fourth or one-sixth of its weight of mercury is added to it at first, and the vessel is placed in cold water, to prevent any rise of temperature from the mutual action. The decomposition of the acid goes on in this manner very slowly, and without any sensible effervescence. When the mercury is dissolved, another portion is added; and this is repeated till the acid has taken up its own weight of metal, or till it is saturated. We thus obtain a solution, in which all the mercury is in the lowest state of oxidation: it is diluted with twenty parts of distilled water, and ammonia is added as long as any precipitate is produced. This precipitate, which is of a very dark colour, is immediately washed with water, and dried on bibulous paper placed before the fire. Its colour becomes lighter, while drying, from the action of the light and air; but it is still of a dark grey, and, when prepared in this manner, is always uniform in its composition.

Mercury is not acted on by muriatic acid, its attraction to oxygen not being sufficiently strong to decompose the water present. It is dissolved by oxymuriatic acid, and when heated strongly in oxymuriatic gas inflames. The gas and the metal, according to one hypothesis, enter into combination, and the compound is chloride of mercury; according to the common theory, the oxygen of the oxymuriatic acid combines with the metal, and the oxide of mercury combines with the acid, thus reduced to the state of real muriatic acid. If any of the oxides of mercury be added to muriatic acid, a combination likewise takes place; or if the acid, or any of its salts, be added to nitrate of mercury, it combines with the oxide, and forms muriate of mercury.

These compounds are different, according to the degree of oxidation of the mercury, or, in the other doctrine, according to the proportion of chlorine. The one, that with the larger proportion of metal, is insipid and inert, and insoluble in water; the other is soluble, and highly acrid.

The production of these compounds is best shewn in the action of muriatic acid on the nitrous solution of quicksilver. If it is added to the solution of mercury made in the cold, and with the diluted acid, the compound formed is principally the insipid and insoluble muriate of the metal; though, from the state of oxidation, there is also often formed a quantity of the other compound, that of the perfect oxide with muriatic acid, which is soluble and acrid, the presence of which is discovered, by pouring off the clear liquor from the insoluble muriate, and adding to it a small quantity of ammonia, when, if any of the soluble muriate is present, a white precipitate is formed, which is a ternary compound of oxide of mercury, ammonia, and muriatic acid. When the solution of mercury in the nitric acid has been prepared by the action of a strong acid, aided by heat, more of the corrosive muriate of mercury is formed, and proportionally less of the other, though there is always a proportion of the latter. In these cases, it is probable that the metal in the solution is in a state of oxidation intermediate between the *maximum* and *minimum*, and that the muriatic acid, by its affinity to the oxide in one or other of these states, causes a change in the state of oxidation, resolving it into the two oxides, from its union with which the corrosive and mild muriates of mercury are formed; the proportions of the corrosive muriate being greater, as the metal is more highly oxidated. Accordingly, if a solution is prepared by adding the perfect oxide of mercury to nitric acid, on adding to this solution muriatic acid, corrosive muriate is alone formed.

These two compounds are very different in their qualities. That with the metal in a high state of oxidation is acrid, corrosive, and soluble in water; the other is mild, insipid, and insoluble. They have both been long used in the practice of medicine, the one under the name of Corrosive Sublimate of Mercury, the other under that of Sweet Sublimate, or Calomel. The former is now named in the Pharmacopœia, Muriate of Quicksilver, the other Sub-muriate of Quicksilver;—names which do not properly denote their composition, and which scarcely distinguish them sufficiently. The terms Proto-muriate, and Deuto-muriate, have been proposed to be applied to them; and on the assumption that they are compounds of chlorine, those of Proto-chloride and Deuto-chloride.

Though these two compounds can be formed in the manner now described, the usual methods of preparing them are different, and are preferable, as being more economical, and as affording more uniform products.

To prepare the corrosive muriate of mercury, the old process was to dissolve 16 parts of quicksilver in an equal weight of diluted nitric acid, with the assistance of heat: the solution being evaporated to dryness, the dry mass in powder is mixed with 20 parts of dried muriate of soda, and 20 of dried sulphate of iron. This mixture is put into an alembic coated with clay and sand, and is sublimed by the heat of a sand-bath. The sublimed matter is the corrosive muriate of mercury.

In this process, the metal is oxidated by the nitric acid; and in the sub-nitrate obtained by evaporation, exists in the highest state of oxidation. When mixed with the muriate of soda and sulphate of iron, and exposed to heat, the sulphuric acid of the sulphate of iron combines with the soda of the muriate of soda: the muriatic acid is disengaged, and is attracted by the oxide of mercury, with which it forms the corrosive muriate. This being volatile, is sublimed by the heat; and being easily condensed, it adheres to the upper part of the subliming vessel. The matter in the bottom of the vessel is the sulphate of soda, mixed with the oxide of iron. The nitric acid combined with the oxide of mercury is expelled by the heat.

A different mode of obtaining this preparation has been introduced into the Pharmacopœia, supposed to be more economical, as the expence of the nitric acid is avoided. One part of quicksilver is boiled with two parts of concentrated sulphuric acid. The metal is oxidated by the sulphuric acid, and then combines with a portion of it: the solution is evaporated to dryness. This dry sulphate of mercury is mixed with four parts of muriate of soda; and the mixture is exposed in a subliming vessel to a sand heat: the sulphuric acid combines with the soda of the muriate of soda, and the muriatic acid of this salt combines with the oxide of mercury. The muriate of mercury is sublimed, and the sulphate of soda remains at the bottom of the vessel. It is doubtful whether this process affords so uniform a result as the other, or rather if it gives so large a product from a given quantity of mercury.

It is corrosive muriate of mercury which is formed by the action of oxymuriatic gas on quicksilver. In the new hypothesis with regard to the nature of muriatic acid, it is regarded as a compound of mercury and chlorine; and in the processes in which it is formed by the action of muriatic acid on oxide of mercury, the acid is supposed to be decomposed, its hydrogen uniting with the oxygen of the oxide, and its chlorine with the metallic quicksilver.

Corrosive muriate of mercury, prepared by the process of sublimation, is in the form of a white compact mass, semi-transparent, and having somewhat of a crystalline arrangement; and when the sublimation has been performed slowly, it is condensed in the form of regular crystals, which are tetraedral prisms. It crystallizes also, from its saturated solution in water in prisms, and likewise, as has been affirmed, in cubes. It is soluble in water, requiring about 20 parts at the temperature of 60° for its solution, and not more than two parts of boiling water. It is also soluble in alkohol, which is capable of dissolving even a larger quantity of it than water does. It changes to a green some of the vegetable colours. Its taste is styptic, and extremely disagreeable; and it acts as a poison, a very small quantity of it inducing inflammation of the stomach, so that it cannot be safely administered but in very minute doses.

This salt is not decomposed by the acids, but is dissolved by them without suffering any apparent change: in such solutions, a ternary combination of the two acids with the oxide of mercury must be formed. It is decomposed by the alkalis. Potash, soda, and several of the earths, throw down a precipitate of a yellow or orange colour, which is a sub-muriate of mercury; or, as Proust affirms, a pure oxide. Ammonia gives a white precipitate. This has been in use as a mild escharotic, under the name of White Precipitate of Mercury. Fourcroy found that it is a triple combination of oxide of mercury, muriatic acid, and ammonia; the proportions being 81 of the first, 16 of the second, and 3 of the last. In its production, the ammonia attracts part of the muriatic acid of the corrosive muriate of mercury, and the oxide is precipitated, retaining a portion of the acid, and attracting a small quantity of the ammonia. When exposed to heat, it is decomposed; ammonia and nitrogen gas being disengaged, and a grey sublimate being obtained, which appears to be imperfect oxide of mercury in combination with muriatic acid, with perhaps a portion of metallic mercury diffused through it, and giving it this colour.

Muriate of ammonia exerts rather a singular action on corrosive muriate of mercury. It renders it much more soluble in water, one part of it rendering nearly five parts of the other soluble in three of water. The two salts remain combined, when obtained solid by crystallization or sublimation, and form a ternary compound of muriatic acid, ammonia, and oxide of mercury. To this compound the alchemists gave the barbarous name of Sal Alembroth. Potash or soda added to its solution, attracts the greater part of the muriatic acid, and the oxide of mercury is precipitated, combined with a portion of acid and of ammonia, forming the same preparation as that obtained by adding ammonia to the solution of the muriate alone; and it is by this indirect process, that that preparation was usually obtained.

Corrosive muriate of mercury is decomposed by sulphuretted hydrogen, by the hydro-sulphurets, and sulphuretted hydro-sulphurets added to its solution: a precipitate is thrown down of a black colour, which appears to be sulphuretted oxide of quicksilver.

It suffers decomposition from a number of the metals. Iron or copper immersed in its solution, abstracts the oxygen partially, and a precipitate is formed, which is the mild muriate. When heat is applied to favour the action of the metals on the corrosive muriate, the decomposition is more complete; both the oxygen and the acid are transferred to the metal employed, and the quicksilver returns to the metallic state. Thus, if two parts of the muriate be mixed with one part of antimony, of arsenic, or of bismuth reduced to powder or to filings, and exposed to heat in a retort, vapours pass into the receiver, which condense into a thick liquid or jelly: this consists of the antimony, or whatever metal may be employed, in combination with the oxygen and muriatic acid of the muriate of mercury; and by continuing the distillation, metallic mercury passes over, or, if the metal employed is one to which quicksilver has an affinity, it retains a portion of it, forming an amalgam. These decompositions take place also with the sulphurets of these metals; and in this case, the mercury remains combined with the sulphur in the state of a sulphuret, or a sulphuretted oxide.

Corrosive muriate of mercury being a salt important from its medicinal use, the precise composition of it has often been an object of investigation. The earlier analyses are necessarily imperfect. Mr Chenevix inferred, that the oxide which is its base is composed of 85 of quicksilver with 15 of oxygen, and that 18 of acid are combined with 82 of oxide: 100 parts of the salt, therefore, consist of 69.7 of quicksilver, 12.3 of oxygen, and 18 of muriatic acid *. Fourcroy and Thenard found the proportions to be 73 of quicksilver, 7 of oxygen, and 20 of acid †. The proportions given on the authority of Zaboada, are 71.5 of quicksilver, 8.5 of oxygen, and 20 of acid ‡. Proust has stated the composition at 80.435 of red oxide, and 19.565 of acid: he obtained from 100 parts decomposed by iron filings, at a high temperature, 74 of quicksilver ||. Dr Wollaston has assigned proportions very nearly the same, 80 of red oxide, composed of 74 of quicksilver, and 6 of oxygen, and 20 of muriatic acid. Adapting these to the hypothesis that this is a chloride of quicksilver, the composition is 74 of quicksilver, and 26 of chlorine. According to this doctrine, the compound contains twice the quantity of chlorine contained in the other chloride: according to the old opinion, the oxide which is the basis of the one contains twice the quantity of oxygen which is contained in the other.

The other muriate of mercury, in which the metal is in a lower state of oxidation, has been long known by the name of Calomel: it may be distinguished by that of mild muriate from its comparative mildness: the name Sub-muriate applied to it is not strictly correct. It has usually been prepared from the corrosive muriate, by bringing an addi-

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* Philosophical Transactions, 1802, p. 156.

† Mémoires d'Arcueil, tom. ii. p. 166.

‡ Journal de Physique, tom. lx. p. 565.

|| Ibid. tom. lxxxi. p. 325.

tional quantity of metallic mercury into combination with its principles. The corrosive muriate is triturated in a glass or stone mortar with nearly an equal weight of pure mercury, the trituration being continued till the mercurial globules are no longer perceptible: the powder is put into a glass matrass, and exposed to a moderately strong heat, applied by the medium of sand. It sublimes, and forms a crust on the upper part of the vessel: this is reduced to powder, and again sublimed; and this sublimation is repeated for a second or third time. The use of these repeated sublimations is to render the combination more perfect, as, at the first sublimation, a portion both of corrosive muriate and of metallic mercury rise unchanged. By trituration, and a second application of heat, this is brought into combination, and the whole resolved into mild muriate. There is perhaps no necessity for more than two sublimations; and when reduced to a fine powder by levigation, it ought to be washed with water, until the water pass off tasteless, by which any corrosive muriate, if present, will be removed.

In this process the quicksilver, added to the corrosive muriate, and enabled by the trituration and application of heat to act upon it, must deprive the oxide, which is the base of that salt, of a portion of its oxygen, and the whole is brought to a lower state of oxidation. The entire quantity of oxide remains in combination with the acid of the corrosive muriate; the mild muriate, therefore, must have a less proportion of acid combined with its base than the other, though it has still a quantity sufficient to produce saturation: and these two salts thus afford an illustration of the general principle, that a metal, when in a high state of oxidation, requires more acid for its saturation than when its oxidation is lower.

The proportions of the elements of the mild muriate have been variously determined by experiment. According to Chenevix's analysis of it, the oxide which forms its base is composed of 89.3 of mercury, and 10.7 of oxygen, and in the salt 88.5 of oxide are combined with 11.5 of muriatic acid. Hence 100 parts consist of 79 of mercury, combined with 9.5 of oxygen, forming 88.5 of oxide, with which 11.5 of muriatic acid are combined. Both in this and in the other muriate, however, the proportion of oxygen to the metal is assigned by this chemist too high. The analysis by Zaboada gives, with regard to both, a smaller proportion of oxygen; the oxide which is the base contains not more than 5 of oxygen in 100 parts, and the compound consists of 89.4 of this oxide, with 10.6 of acid: its ultimate principles are 85 of quicksilver, 4.4 of oxygen, and 10.6 of muriatic acid *. Its analysis by Fourcroy and Thenard gives as the proportions, 83 of quicksilver, 5.4 of oxygen, and 11.6 of muriatic acid †. Proust gives the proportions of 86.94 of black oxide, and 13.06 of acid. When decomposed by iron-filings at an elevated temperature, it affords, he states, 84 of quicksilver from 100 parts ‡. Dr Wollaston adopts the proportions of 85 of mercury, 3.5 of oxygen, and 11.5 of muriatic acid. Considering it as a chloride, these last give the proportions of 85 of mercury, and 15 of chlorine. According to the proportions established by any of these analyses, more mercury is employed in the process for converting corrosive into mild muriate, as given in the Pharmacopœias, than enters into the combination, and it must therefore be attended with loss.

Another mode of preparing mild muriate of mercury was proposed by Scheele. It consists in dissolving quicksilver in an equal weight of diluted nitric acid, promoting the solution by the application of heat: muriate of soda, in quantity equal to rather more than half the weight of the

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* Journal de Physique, tom. lx.

† Mémoires d'Arcueil, tom. ii. p. 166.

‡ Journal de Physique, tom. lxxxi. p. 325.

quicksilver, is dissolved in boiling water, and into this, while warm, the solution of nitrate of mercury is poured. A precipitation takes place; the clear liquor is poured off, and the precipitate is washed with water until the water pass off tasteless. In this process the mercury is oxidated and dissolved by the nitric acid; and on adding the solution of muriate of soda, the soda combines with the nitric acid of the mercurial solution, while the muriatic acid unites with the oxide of mercury. The same product is obtained by adding muriatic acid alone to the nitrate of mercury; but it is better to use muriate of soda, the soda of which saturates the nitric acid, which otherwise, when disengaged uncombined, acts on the mercurial oxide, and communicates to it a portion of oxygen.

From the nature of this preparation, it is obvious, that the mercury in the nitrous solution ought to be in the lowest state of oxidation, as it is only in this state that it forms the mild muriate; and if more highly oxidated, a portion of corrosive muriate will be formed. When Scheele proposed the process, the theory of metallic solutions was imperfectly understood; and on the supposition, that by boiling the acid on the metal, it would be more completely saturated with it, he directed the application of heat. From this, one source of error is introduced into the process: there is such an excess of oxide in the solution, that the mere affusion of water precipitates a portion of insoluble sub-nitrate; and hence, when the solution of mercury is poured into the solution of muriate of soda, the water of the solution throws down a quantity of this sub-nitrate, mixed with the precipitate of the portion of muriate that is formed. But besides this, the metal is more highly oxidated, and the solution gives less mild muriate, and more corrosive muriate, than the solution does that is formed in the cold. This has been doubted by some chemists, from the circumstance, that the additional portion of mercury which the heat causes to be dissolved, is taken up without effervescence; and hence it has been inferred, that none of the acid is decomposed, so as to oxidate the metal more highly. The fact however is, that more corrosive muriate of mercury is formed, when the solution of mercury has been prepared with heat, than when the one prepared in the cold is employed, as I have often found on experiment. And if the process of Hahneman, for preparing the solution of nitrate of mercury in the cold, already stated, be followed, scarcely any corrosive muriate is produced, but the whole is converted into mild nitrate. With attention to this circumstance, this process may be employed for the formation of this preparation, but it has no advantage over that by sublimation, and, as liable to furnish a less uniform product, it ought to be discarded. As usually prepared, it is a mixture of mild muriate and of sub-nitrate of mercury; and if not very carefully washed, a portion even of corrosive muriate may be mixed with it*.

When mercury is heated strongly by the contact of wires from a galvanic battery in muriatic acid gas, the mild muriate is formed, and hydrogen to the amount of half the volume of the acid gas is evolved.

Mild muriate of mercury prepared by sublimation, is in the form of a dense mass, of greater specific gravity than the corrosive muriate, that of the one being 5.1398, of the other 7.1758: it has a yellowish tinge, while the corrosive muriate is white. It displays a crystalline structure; the mass being composed of an aggregate of short prisms, and when sublimed slowly, it condenses in tetraedral prisms acuminated by four planes, or in octaedrons. When in its dense state, it has a slight degree of ductility, and is semi-transparent. It is volatile, but rather less so than the corrosive muriate. It is so little soluble, as to require,

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* It is singular that this process is given very distinctly in the edition of the London Pharmacopœia 1650, a period at which it could scarcely have been expected to have been proposed.

according to Rouelle, 1152 parts of water for its solution. It is mild and insipid, and as a medicine has much less activity than the corrosive muriate, though better adapted by its operation to many medicinal purposes, and therefore more extensively employed.

It is dissolved, though with difficulty, in the muriatic acid: oxymuriatic and nitro-muriatic acids, by affording oxygen to its oxide, convert it into corrosive muriate. The alkalis decompose it by abstracting its acid. Potash, soda, or lime in solution, triturated with it in powder, gives it a greyish colour. Ammonia renders it perfectly black; the ammonia, while it separates the oxide of mercury, still farther de-oxidating it. This black matter is very similar to the grey oxide thrown down by ammonia from that solution of mercury in nitric acid in which the metal is in a low state of oxidation.

It does not appear that muriatic acid combines with mercury in any state of oxidation intermediate between those oxides which afford the mild and the corrosive muriates. When added to a mercurial salt, in which the metal is in an intermediate state, the acid does not combine with the oxide, but resolves it into these two oxides, with which it unites. Or if a portion of metallic quicksilver is added to the corrosive muriate, inferior to that requisite to change the whole of it into mild muriate, there is no intermediate compound; but, with a portion of mild muriate, a quantity of corrosive muriate is sublimed.

Chenevix inferred, that an oxymuriate, or, as he considers it, a hyper-oxymuriate of mercury, may be formed, by transmitting a current of oxymuriatic acid gas through water, in which red oxide of mercury is suspended. The oxide becomes of a dark brown colour, and a solution takes place. On evaporating to dryness, a great proportion of corrosive muriate was found in the mass; but by separating the last formed crystals, some hyper-oxygenized muriate of mercury was obtained: on crystallizing it a second time, it was obtained nearly pure. This salt is more soluble than corrosive muriate; about four parts of water retaining it in solution. Acids poured on it disengage the usual smell of hyper-oxymuriatic acid, and the liquor becomes of an orange colour *.

Mercury is not acted on by any of the other acids, but its oxides combine with them. These may be formed, either by digesting the acid on the oxide, or by adding to a solution of nitrate of mercury a solution of a salt containing the acid with which the oxide of mercury is to be combined: a complex affinity produces a mutual decomposition, and two new combinations. Thus, if a solution of phosphate of soda be added to a solution of nitrate of mercury, the soda combines with the nitric acid, and phosphate of mercury is precipitated: and similar decompositions are effected by the greater number of the other neutral salts. The combinations thus obtained, must vary according to the state of oxidation of the mercury in its nitrous solution: but it is principally those salts formed with the imperfect oxide that have been taken notice of, as it is the solution in which this oxide exists, that generally affords precipitates with the acids.

Of the salts which can be introduced in this place, the phosphate, the preparation of which has just been described, is in the form of a white precipitate, insoluble in water, mild and insipid. It is said to be phosphorescent, and, when exposed to a high temperature, is decomposed, affording phosphorus. The fluate of mercury is in the form of a white precipitate, insoluble. The borate is of a yellowish colour. The carbonate of mercury, formed by the addition of carbonate of potash or soda to the solution of nitrate of mercury, is of a white colour, with a shade of

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* Philosophical Transactions, 1802, p. 160.

yellow; and its formation is very well shewn by this colour, as the precipitate by pure potash or soda is of a deeper colour.

Iodine acts readily on quicksilver; according to Gay Lussac two compounds are formed; one yellow, the other red; both are fusible and volatile, and insoluble in water. The yellow contains half the quantity of iodine in the other. Hydriodate of soda added to a mercurial solution in the first degree of oxidation, throws down a yellowish green precipitate; from a solution at the maximum of oxidation, it throws down one of an orange red.

The oxides of mercury precipitated from their combinations with the acids, by the alkalis or earths, especially by ammonia or lime, Bayen discovered, are capable of having a detonating quality communicated to them, by combination with sulphur. If triturated with one-sixth of their weight of sulphur, on being exposed to heat, they explode. It is an essential circumstance in their preparation for this purpose, that they be dried in the open air, and exposed to the light *.

Another fulminating preparation of mercury, of greater power, was discovered by Mr Howard. In making some experiments, in which red oxide of mercury had been mixed with alkohol, and afterwards nitric acid added, a precipitate was formed, to which, after it was dried, sulphuric acid having been added, a violent explosion unexpectedly took place. The process which he found, after a variety of experiments, to succeed best in preparing this fulminating mercury, was to dissolve 100 grains of mercury in an ounce and a half of nitric acid by measure: the solution, when cold, is *poured upon* two ounces by measure of alkohol: a moderate heat is to be applied till an effervescence is excited; a precipitate is formed, which is to be immediately collected on a filtre, washed with distilled water, and

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* Opuscules Chimiques, tom. i. p. 346.

carefully dried in a heat not much exceeding that of a water-bath. From 100 grains of mercury, about 120 or 130 grains of dry precipitate are formed. According to Brugnatelli, it may also be prepared without heat, by pouring on yellow sub-sulphate of mercury, about four times its weight of alkohol, and five times its weight of nitrous acid, an effervescence taking place, and the concrete matter being fulminating mercury *.

This preparation fulminates strongly. If two grains of it be laid on an anvil, and struck smartly with a hammer, it explodes with a loud report. Three or four grains occasion indentations in the hammer and anvil. The shock of an electrical battery has the same effect, as has also strong friction, exposure suddenly to a heat equal to 368° of Fahrenheit, or the contact of sulphuric acid. It does not explode spontaneously, and is therefore less dangerous than several other fulminating powders. Its initial force is much greater than that of gun-powder, but does not extend so far. From this property it is well adapted to the blasting of rocks.

Mr Howard found this powder to consist of oxide of mercury, combined with oxalic acid, and nitrous etherized gas,—the two latter being produced by the action of the nitric acid on the alkohol. It contains about 65 of mercury in 100 parts. Its explosion he supposes owing to the oxygen present combining with the carbon and hydrogen, forming watery vapour and carbonic acid: nitrogen gas is also discharged, and much caloric is evolved, so as to volatilize the mercury. It is to this latter cause principally,—the conversion of the mercury into vapour, that Mr Howard ascribes its great elastic force; and his experiments shew that such a cause exists; since, when the detonation was performed in close vessels, a film of mercury covered the internal surface, and mercurial vapour, it is

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* Philosophical Magazine, vol. xvi., p. 186.

known, has a great elastic power*. According to Berthollet, however, fulminating mercury does not contain oxalic acid, but ammonia and alkohol somewhat altered†.

Quicksilver combines with sulphur. When equal parts of them are triturated together, the mercurial globules soon disappear, nor can they be distinguished by the microscope, if the trituration has been sufficient. This, therefore, must be regarded as a chemical combination: it is promoted by heat, and is effected more speedily by pouring the mercury into the sulphur melted. This compound, formerly known by the name of Mineral Ethiops, is termèd Black Sulphuret of Mercury, to distinguish it from another compound, the Red Sulphuret. This is prepared by mixing one part of sulphur with from seven to eight parts of mercury. The black powder which they form is exposed to a heat sufficient to inflame it: after the inflammation has ceased, the remaining mass is sublimed in close vessels. The sublimate is mercury in combination with sulphur: it is of a very fine red colour, and, when levigated, is in common use as a pigment, under the name of Cinnabar, or Vermilion. The preparation of it is attended with difficulty, as to the production of the fine red colour. Mr Tuckert and M. Payssé have given the details of the process, as it is carried on in Holland, on a large scale‡.

Mercury decomposes the alkaline sulphurets, when these are dissolved in water, attracting the super-sulphuretted hydrogen, and forming a black powder, similar in appearance to black sulphuret of mercury. Some of these compounds, especially that precipitated from the sulphuret of ammonia, assume a red colour by exposure to the air, probably from the absorption of oxygen, which combines with

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* Philosophical Transactions, 1800, p. 204.

† Philosophical Magazine, vol. xii. p. 92.

‡ Annales de Chimie, tom. iv. and tom. li.

their hydrogen. This change is accelerated by trituration, and the application of a moderate heat; and on this principle a method has been proposed of forming cinnabar in the humid way. It consists in triturating mercury and sulphur with potash and water, the vessel being kept warm in a sand-bath. After two hours trituration, the colour changes from a black to a brown; it then passes rapidly to a red, and forms cinnabar *. According to Guibourt, the black sulphuret is formed when sulphuretted hydrogen is made to act on proto-muriate of quicksilver, the hydrogen uniting with the oxygen of the oxide, and the sulphur with the metal. When sulphuretted hydrogen is transmitted through a solution of corrosive muriate, a black precipitate is formed; which, when sublimed, changes entirely into cinnabar: the other, when heated, affords cinnabar and quicksilver.

Both the black and the red compounds have been supposed to contain the metal in an oxidated state: and Vauquelin ascribed the fine red colour of cinnabar to the large quantity of oxygen with which the mercury is combined †. This opinion, however, does not appear to be just; they are pure sulphurets. According to Proust, cinnabar consists of 85 of mercury, with 15 of sulphur; or 100 with 17.6 ‡. According to another analysis, the proportions are 86.7 of mercury, with 13.3 of sulphur, or 100 with 15.4 ‖. These last correspond nearly with those which would be inferred from the relative combining weights of oxygen and sulphur, and the proportion of oxygen with which mercury combines, that is, 100 with 16. And in an analysis by Guibourt, these are stated as the proportions. The proportions in the black sulphuret, according to the common mode of preparation, must be indeterminate. According

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* Nicholson's Journal, 4to, vol. ii. p. 1.

† Ibid. vol. v. p. 311. ‡ Ibid. 8vo, vol. i. p. 112.

‖ Philosophical Magazine, vol. xii. p. 279.

to Guibourt, this compound is formed by the action of sulphuretted hydrogen on proto-muriate of mercury; and when decomposed by being heated with iron, it yields 100 of mercury from 108.2 of sulphuret *.

Mercury does not seem capable of uniting with carbon. It combines with phosphorus, though with much difficulty. To effect the combination, Pelletier employed the following process. Two parts of the red oxide, or rather subnitrate of mercury, and one and a half of phosphorus, were mixed together, covered with water, and heated in a glass vessel. The phosphorus attracts the oxygen from the oxide: part of it is converted into phosphoric acid, another portion of it combines with the reduced mercury. This phosphuret of mercury is a tenacious concrete substance, fusible and easily decomposed.

Quicksilver combines with many of the metals. All these combinations are brittle or soft; and if the quicksilver is in considerable proportion, are more or less fluid: they are named Amalgams. The metal of potash appears to exceed all others in rendering mercury solid, one part of potassium giving the solid form to 70 parts of quicksilver. It has not been found possible to unite it with iron, cobalt, or nickel, probably from the great infusibility of these metals, counteracting the weak affinity they may have to the quicksilver. It unites with difficulty with platina; but when the precipitate from the solution of platina in nitro-muriatic acid is used, according to the process of Moussin Poushkin, the union is effected more easily. The alloy is brilliant, and of a fine grain †. The combination with gold is effected with facility: the amalgam is more or less solid, according to the proportion, and of a yellow colour; when solid it is easily fused, and crystallizes on becoming concrete in quadrangular prisms or octaedrons. By a

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* Annales de Chimie et Physique, tom. i. p. 425.

† Nicholson's Journal, 4to, vol. i. p. 539.

strong heat the mercury is volatilized. Silver amalgamates with equal facility; the amalgam varying in consistence according to the proportions, and being of a dull white colour. When solid, it is crystallizable. The specific gravity of the compound always exceeds greatly the mean specific gravities of the two metals, and has even been said to be superior to that of quicksilver itself. From its property of amalgamating with gold and silver even in the cold, mercury is used to separate these metals from the substances with which they are mixed. It is thus capable of extracting the hundred-thousandth part of gold. In gilding and silvering, it is, from the same property, the medium of union between the gold or silver, and the metal on which the operation is performed.

Mercury is extensively used for these purposes. Its amalgam with tin is used in the silvering, as it is termed, of mirrors. By its application in the barometer, it has demonstrated the weight of the atmosphere; and, from the regularity of its expansion, it is the best thermometrical fluid. In medicine it is extensively employed.

The mercury of commerce often requires to be purified; it is even frequently adulterated. Lead is added to it, and the addition of a little bismuth renders this alloy more fluid and mobile, probably by increasing its fusibility. The adulteration is suspected, when the quicksilver, after it has been strained through leather, tarnishes quickly; when it does not divide readily into globules; or when these do not preserve exactly the globular form, nor unite readily when brought near to each other. It can be detected with certainty by heating it in an iron spoon, when, if any metal be present, it will be the residuum. It is purified by distilling it from iron-filings; or to a certain extent by agitation in the air, the alloy in the latter case separating in an oxidated state.

CHAP. IX.

COPPER.

THIS metal is of a red colour, with a shade of yellow. It is inferior in lustre, malleability, and ductility, to the more precious metals. Being more abundant, and being easily cast and worked, it is applied to many useful purposes, and its value would be greater, were it not acted on by air and moisture, and were it not noxious to health. It is found in many countries, and is one of those metals which were of earliest discovery. It exists native, and mineralized by oxygen, by sulphur alone, or in combination with iron, arsenic, antimony, and other metals, and by a number of the acids.

The sulphurets are the ores from which it is usually extracted. The ore is roasted by a low heat in a furnace with which flues are connected, leading to a chamber in which the sulphur that is volatilized is collected. The remaining ore is smelted in contact with the fuel; the iron present in the ore, not being so easily reduced or fused as the copper, remains in the scoriæ: the copper often requires repeated fusions, and even after these, is still alloyed with portions of those metals which may have been present, which are not volatile, and are of easy fusion. Hence, the copper of commerce is never altogether pure, but generally contains a little lead, and a smaller portion of antimony. The carbonates of copper reduced by fusion, in contact with the fuel, afford a purer copper. The solution of sulphate of copper which is met with in some mines, does so likewise, the copper being precipitated in its metallic state, by immersing in it pieces of iron, and the precipitate of copper being fused.

This metal has a specific gravity of 7.78; which is increased by hammering to 7.87: and it has been stated so high as 8.8, or even 9. In hardness, it is inferior to iron and platina, but superior to the greater number of metals. Its ductility is such, that a wire one-tenth of an inch in diameter, can support a weight of 299 libs. It is so malleable, that it can be beat into very thin leaves. It has a sensible odour when rubbed, and its taste is disagreeable and metallic.

To melt copper, it requires to be exposed to a strong white heat, equal to 27 of Wedgwood. If slowly cooled, it is obtained in crystals, which are single or double tetraedral pyramids. By a more intense heat it is volatilized.

If copper be heated in contact with atmospheric air, even below the temperature of ignition, its surface exhibits ranges of prismatic colours, which, as the heat is continued, change quickly,—appearances probably owing to incipient oxidation. When the temperature is raised to ignition, thin scales of a brown colour form on its surface. These are easily detached, by dipping the copper in cold water: when exposed to a continued heat, they become of a deep-red colour, probably from the farther absorption of oxygen. When copper is exposed to a very high temperature, it burns with a green-coloured light. This is bright when the copper is placed in a kindled stream of oxygen and hydrogen gases: it is also exhibited when it is subjected to a red heat with nitre. There appear to be two definite degrees of oxidation of copper. According to Chenevix, the metal, in the first degree of oxidation, is not obtained by the action of atmospheric air on it at a high temperature, but exists in some of its saline combinations, from which it may be separated; as, for example, dissolving copper in muriatic acid, with the assistance of heat, adding to the solution a portion of metallic copper, and excluding the access of air. The solution becomes of a dark-brown colour, and on adding potash, an orange-coloured precipitate is thrown down. This he regarded as the oxide at the minimum, containing in 100 parts 11.5 of oxygen, or in which 100 are combined with 12.9 *. This oxide forms the principal part of the red copper ore. Proust supposed that the oxidation to the maximum is effected by the action of atmospheric air at a high temperature; the scales formed on the surface of the metal, consisting of this oxide, with an intermixture of metallic copper, which may be also oxidated, when the application of a red heat is continued for some time to the scales reduced to powder. This oxide, the black, as Proust names it, to distinguish it from the red, is also precipitated from the salts of copper, and is obtained in the state of a black powder, by exposing the precipitate to a heat sufficient to expel the water in combination with it †. It consists, according to his analysis of it, of 80 of copper, and 20 of oxygen, or 100 with 25. Berzelius has assigned almost precisely the same proportions to these oxides, stating the two at 100 of metal, with 12.5, and 25 of oxygen ‡.

From the salts of copper precipitates are thrown down by the alkalis, and some of the earths, which are of a green or blue colour, of various shades, and were formerly regarded as oxides. According to Proust, the green is a sub-salt, or an oxide with a small portion of acid, and a quantity of water; the blue, a compound of the black oxide, with water alone, and therefore a Hydrate of Copper. This water is in the proportion of 24 in 100 parts: he considers it as in a state of chemical combination, and as the cause of the blue colour; and this hydrate he supposes to

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* Philosophical Transactions, 1801, p. 255. 257.

† Annales de Chimie, tom. xxxii. p. 26.

‡ Philosophical Magazine, vol. xli. p. 200.

be the base of a number of the salts of copper. These opinions were adopted by Chenevix, in his researches on the arseniates of copper *. Berthollet *junior* has shewn, however, that the blue precipitate contains a portion of acid, or is a sub-salt. Still the oxides of copper appear to have a strong attraction to water, and to retain a considerable portion of it in combination.

Copper, at its maximum of oxidation, is semi-vitrified by a strong heat, acquiring lustre, and a deep red colour. Its oxides are not decomposed by heat alone; but at a high temperature, charcoal, and substances containing carbonaceous matter, attract the oxygen.

When exposed to humidity, and to the action of air, its colour tarnishes, and it is soon covered with a green efflorescence or crust. This is carbonate of copper.

Copper is acted on by the greater number of the acids, and saline combinations are formed generally soluble and crystallizable, and of a green or blue colour. Ammonia throws down from them a blue precipitate, and, added in excess, re-dissolves it, forming a transparent solution of a very deep blue colour. Iron, immersed in any of these solutions diluted, precipitates metallic copper.

Sulphuric acid, concentrated and aided by heat, oxidates and dissolves copper; and when diluted, acquires from it even in the cold a blue colour, indicating that a portion is dissolved. The sulphate of copper is obtained by crystallization in the form of rhomboidal prisms; their colour is a rich blue: they are transparent, but become opaque from efflorescence on exposure to the air: they are soluble in about four parts of water at 60°, and in two parts at 212°; the taste of this salt is harsh and styptic, and it possesses a degree of corrosive power. It is the Blue Vitriol of commerce, and is generally obtained not by the solution of copper in sulphuric acid, but is either

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* Philosophical Transactions, 1801.

crystallized from the solution of it found in copper-mines, or is formed by roasting copper pyrites, and exposing the residual matter to the action of air and humidity: by the roasting, the sulphur is partially dissipated, and the relative increase thus effected in the proportion of metal, favours the oxidation of the compound; sulphate of copper is slowly formed, and is extracted by lixiviation and crystallization.

Sulphate of copper is decomposed by heat. It fuses from the water of crystallization; when this is dissipated, a light blue powder remains, which, urged by a stronger heat, gives out its acid, the oxide of copper remaining of a black colour. From the analysis in this mode, Proust infers, that its constituent parts are, black oxide of copper 32, sulphuric acid 33, and water 36 *, which agrees nearly with the estimate before made by Mr Kirwan, in which the proportions had been stated at 40 of oxide, 31 of acid, and 29 of water. The water expelled by heat, Proust and Chenevix supposed not to be water of crystallization, but water combined with the oxide of copper, forming a hydrate; and, according to the latter chemist, sulphate of copper is composed of 42 hydrate of copper, 23 of acid, and 25 of water.

Potash added to a solution of sulphate of copper, taking care to avoid adding it in excess, throws down a precipitate of a green colour, which is a sub-sulphate, consisting, according to Proust, of 68 parts of black oxide of copper, 14 of water, and 18 of sulphuric acid. Ammonia throws down from the sulphate, as it does from all the salts of copper, a precipitate of a greenish or blue colour according to the quantity, and, when added in excess, it re-dissolves this, forming a solution, transparent, and of a deep blue colour.

Sulphurous acid, though incapable of dissolving copper,

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* Annales de Chimie, tom. xxxii. p. 55.

combines with its oxide; or the combination may be more easily effected, by adding a solution of sulphite of potash, to a solution of nitrate of copper. A yellowish precipitate is first formed, and afterwards crystals are deposited of a greenish white colour: the former contains an excess of oxide; the latter is the sulphite of copper: it is sparingly soluble in water, is decomposed by heat, and by the affusion of sulphuric acid, sulphurous acid gas is disengaged. According to Chevreul, the former is a triple compound of sulphurous acid, potash, and oxide of copper. And the proper sulphite of copper is formed by the action of sulphurous acid on black oxide of copper; one part of the acid abstracts oxygen from the oxide, and forms sulphate of copper, while the other combines with the oxide at the minimum of oxidation, and forms the sulphite, which may be obtained by evaporation of its solution in small crystals of a fine red colour *.

Nitric acid acts on copper with rapidity. Even in the cold nitric oxide gas is disengaged. When the acid is diluted, a similar production of nitric oxide takes place, especially when its action is promoted by heat. The oxide combines with a portion of the acid, and a solution is formed of a green or blue colour, according to the degree of oxidation; a portion of a yellowish-brown powder generally remaining undissolved. By evaporation, this solution affords prismatic crystals of a blue colour, soluble in water, and deliquescent: exposed to heat, nitrous acid vapour is exhaled, as soon as the salt is in fusion, and the greater part of the acid is decomposed or disengaged. From the facility with which this salt parts with oxygen, it acts with energy on a number of substances. It detonates slightly when thrown on burning fuel; and when struck with phosphorus, detonates more loudly. It is capable of burning some of the metals. A singular action of this

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‡ Annales de Chimie, tom. lxxxv. p. 181.

kind, which it exerts on tin, has long been known. If a quantity of the crystallized salt in powder be wrapped up in tinfoil, nitrous acid vapour is disengaged, the temperature rises, and the metal is inflamed, owing to the transfer of the oxygen from the copper to the tin, this latter metal having a strong attraction to oxygen, and combining with a large quantity of it. The salt, to produce this effect, must be somewhat humid; if perfectly dry, there is no action, and the experiment has often been adduced as a proof of the chemical axiom, that bodies must be fluid, or at least humid, to enable them to act on each other. I have found, however, that it depends on a different cause, that of the water modifying the action of the acid; for if the solution be concentrated by evaporation, and the salt employed while from the temperature it is soft and even humid, it does not act on the tin, until a little water is added. It is therefore an example of the fact already noticed, established by more direct experiments, that nitric acid does not act on metals if highly concentrated, but requires the presence of water.

Nitrate of copper is decomposed by the alkalis, with results similar to those observed in the decompositions of sulphate of copper. Potash or soda throws down a blue precipitate, which becomes green when the mixture is agitated, if an excess of alkali has not been added. If, on the other hand, the nitrate is added to the solution of potash much diluted, a precipitate is obtained of a bright blue colour. The green precipitate, according to Proust, is a sub-nitrate of copper. Sulphuric acid disengages from it nitric acid, as does also the application of heat. It differs in nothing from a sub-nitrate obtained by distilling nitrate of copper in a glass retort, until it form a thick insoluble matter, and which, according to Proust, consists of 67 of black oxide of copper, 16 of nitric acid, and 17 of water. If the application of heat be continued to it, or if it be boiled with a solution of potash, the whole of the acid is abstracted, and it is brought to the state of the black oxide.

The blue precipitate is regarded by Proust as oxide of copper, combined with 14 or 15 parts of water in 100: and it is equally obtained from the other salts of copper by decomposing them, by the addition of a sufficient quantity of alkali. To obtain it pure, it is necessary to dilute it in a large quantity of boiling water, to withdraw the water by filtration, and wash the precipitate largely. It is then of a fine blue colour. If spread on paper, and heated until the temperature is above 212°, it loses its colour, becomes green, and is converted into the black oxide,—a change ascribed to the loss of its water. 100 grains of it distilled, give 24 of water, 75 of black oxide, and about a grain of carbonic acid, which may be regarded as accidentally present. This substance, though permanent in the air, decomposes gradually when kept under water. It dissolves with facility in acids. It is also dissolved by a strong solution of potash, and very readily by ammonia. This hydrate of copper Proust supposes to exist in nature, and to be the base of the blue copper ore; and the same opinion was adopted by Chenevix.

The opinion that this blue precipitate, obtained by the action of the fixed alkalis from the nitrate, as well as from other salts of copper, is a hydrate, and not a sub-salt, seems to be incorrect. Berthollet *junior* examined it *, as obtained from the different salts of copper, and found that it always retains a portion of the acid of the salt, and is equally a sub-salt with the green precipitate, differing only in the proportion of acid being less. Thus, the sulphuric being an acid which is more easily detected by re-agents than the nitric, he precipitated sulphate of copper by potash, washed the precipitate with great care, and dried it

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* Chemical Statics, vol. ii. p. 484.

slowly. On dissolving 100 parts of it in muriatic acid, and adding muriate of barytes, a precipitate was afforded, which indicated the presence of seven parts of sulphuric acid. In like manner, when the blue precipitate is digested with an alkali until it lose its colour, the alkali, saturated with muriatic acid, gives a precipitate with muriate of barytes of the same weight as the preceding, and the black oxide remaining weighs 72 parts from 100 of the precipitate. Hence the blue precipitate, analysed in this way, the hydrate of copper of Proust, consists of 72 oxide of copper, 7 of sulphuric acid, and 21 of water. The green precipitate from sulphate of copper, contains 18 of acid, and 14 of water. When the blue precipitate was decomposed by heat, in the manner that Proust made his analysis, a portion of acid was found retained by the oxide, which was detected by dissolving this oxide in muriatic acid, and adding muriate of barytes. And Berthollet also found, that by boiling this precipitate strongly and repeatedly in water, a part, though not the whole of its acid, may be abstracted, and it changes its colour from a blue to a brown. The blue precipitates from the other salts of copper, this chemist found equally to contain portions of the respective acids. Those obtained from the nitrate and muriate of copper, exposed on burning fuel, exhaled vapour, as they did also from the affusion of sulphuric acid, which indicated the presence of nitric and muriatic acids. And the precipitate from muriate of copper, dissolved in nitric acid, gave a precipitate too with nitrate of silver. These experiments must be regarded as decisive. Oxide of copper, however, does appear to have a stronger affinity to water than most of the metallic oxides; as the precipitates of its salts, even in their dry state, retain more of it than those of the others do, and as it exists in considerable quantity in several of the native combinations of copper.

The precipitate obtained from nitrate of copper by lime, levigated with the addition of from 5 to 10 of lime in 100 parts, forms the paint known by the name of Verditer.

Muriatic acid dissolves copper slowly when the atmospheric air is admitted, and with more facility when its action is promoted by a moderate heat, hydrogen gas being in the latter case disengaged. The solution is of a green colour. A similar solution, more concentrated, is obtained by adding oxide of copper to muriatic acid. The solution is of a deep green colour, and by evaporation affords slender prismatic crystals of a grass-green colour. This salt is acrid; deliquescent; and very soluble in water. It is fused with a moderate heat, and by an increase of heat may be decomposed: the acid receiving a portion of the oxygen of the oxide, is disengaged in the state of oxymuriatic acid; while the copper remains at a low state of oxidation, retaining a portion of acid. The alkalis decompose it nearly in the same way as the other salts of this metal. Potash throws down a green precipitate from its solutions, which, by the farther action of the alkali, may be rendered blue; these precipitates being sub-muriates of copper. Proust, estimating the quantity of oxide which muriate of copper contains from the quantity of oxide obtained by the action of potash, and of acid from the precipitate afforded by nitrate of silver, infers that it consists of 40 parts of the black oxide, 24 of acid, and 36 of water.

Besides this, there are other combinations of copper with muriatic acid, in other states of oxidation. If a quantity of copper-filings be added to a solution of green muriate of copper, and the phial be closed, so as to exclude the atmospheric air, the solution becomes nearly colourless: the metallic copper has, therefore, shared the oxygen of the oxide of copper, which was in combination with the acid. But that a portion of this imperfect oxide is still in solution, is evident from this, that on admitting the atmospheric air the liquor regains its colour, and the tint appears first at the surface. This denotes, therefore, a combination of copper in a low state of oxidation with muriatic acid. Chenevix found, that by mixing black oxide of copper, with nearly its own weight of metallic copper precipitated from its solution by iron, on adding to the mixture muriatic acid in a phial accurately closed, the whole nearly was dissolved, forming a solution of an orange-brown colour; and as the metallic copper could receive the oxygen necessary to its combination with the acid only from the black oxide, the whole must have been in a lower state of oxidation. And Proust had observed, that recently prepared muriate of tin, added to a solution of muriate of copper, deprives it of a portion of its oxygen, and a white muriate of copper is formed *. This muriate is also produced, according to Berthollet *junior*, by adding a little water to the brown muriate of copper, which, by the affinity of the water, is made to pass to two states of oxidation, that forming the white muriate which is precipitated, and a blue muriate which remains dissolved, giving its colour to the solution. The white muriate has probably a deficiency of acid, which renders it insoluble, for an addition of acid dissolves it, forming a colourless solution †. It seems to consist of 74 oxide of copper, and 26 of acid.

Oxymuriatic and nitro-muriatic acids dissolve copper; and as the solution proceeds in the latter acid, a green powder is precipitated, which, according to Proust, is a sub-muriate. Chenevix found, that on passing oxymuriatic acid gas through water in which oxide of copper is suspended, the oxide is dissolved. Copper in thin leaves burns in this gas; the product is partly solid and fusible, and partly volatile. A product analogous to the first is formed by heating copper with corrosive muriate of mer-

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* Annales de Chimie, tom. xxviii. p. 218.

† Chemical Statics, vol. ii. p. 491.

cury. From its appearance, it was named Resin of Copper by Boyle. It melts at a heat inferior to redness, and forms a semi-transparent yellowish mass, sometimes exhibiting a crystallized structure; it is not decomposed or sublimed by a strong red heat in close vessels; if air is admitted, it is dissipated in white fumes; is insoluble in water; effervesces in nitric acid; dissolves in muriatic acid, and is precipitated by the affusion of water unaltered; is decomposed by potash, affording prot-oxide of copper. This substance is analogous to the white muriate of copper. According to the theory of its being a compound of chlorine, it is the proto-chloride; and according to Dr J. Davy's analysis of it, consists of 64 of copper, and 36 of chlorine. The volatile sublimate, which is also formed in the action of oxymuriatic gas on copper, is, according to the same doctrine, a chloride, containing a larger proportion of chlorine, as it is formed by heating the other in the gas; it is also produced by evaporating the deliquescent green muriate slowly to dryness; and, according to the same authority, is composed of 47 of copper, and 53 of chlorine *.

Chloric acid, according to Vauquelin, dissolves per-oxide of copper, and forms a solution of a green colour, containing a slight excess of acid, which crystallizes with difficulty; the salt is deliquescent, and communicates to inflammable bodies in burning a fine green flame †.

The other mineral acids, though they do not easily dissolve copper, so as to produce neutral compounds, combine with its oxides. These combinations are most easily obtained, by adding to a solution of nitrate of copper any compound salt, containing the acid with which the oxide of copper is designed to be combined. Thus, the precipitate thrown down by carbonate of potash from a solution of nitrate or sulphate of copper, is carbonate of copper.

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* Philosophical Transactions, 1812.

† Annales de Chimie, tom. xcv.

When there is no excess of acid or alkali, it is insoluble, and of a fine green colour. It is decomposed by heat: from the products of its decomposition, Proust states its composition at 70 of black oxide of copper, 25 of acid, and 5 of water. Native carbonate of copper exists, of a green and blue colour, crystallized. Phosphate of Copper, obtained by a similar process, is in the form of a greenish precipitate: it consists, according to Chenevix, of 49.5 oxide of copper, and 12 of water, combined with 35 of acid, and 3.5 of water of crystallization. Borate of Copper is of a similar colour, and very little soluble. The Fluate can be formed by the solution of oxide of copper in fluoric acid, and can be obtained crystallized. With some other acids oxide of copper combines, as with the arsénic acid, forming a compound of a fine green colour, used as a pigment; and with the acetic acid, forming verdigrease. These combinations are to be afterwards noticed.

Iodine acts on copper when they are heated together: the compound is insoluble in water. The precipitate from a salt of copper by an alkaline hydriodate, is of a greyish white colour.

The alkalis decompose the salts of copper, with results which have been in a great measure stated in the preceding paragraphs. Ammonia added in excess re-dissolves the oxide, forming a ternary compound. It can also combine directly with the oxides of copper. If the metal be highly oxidated, the solution is of a deep blue colour: if at an inferior degree of oxidation, it is colourless. This is proved by an experiment similar to that stated with regard to the muriate of copper. If ammonia be poured on copper-filings, and exposed to the air, it acquires a blue colour; but if the phial containing them be closed, the colour of that portion of the liquid immediately above the undissolved copper gradually disappears, and the whole at length becomes colourless. If the air be now admitted, the surface of the liquid in a few minutes assumes a blue tint, which deepens and extends through the whole. The metallic copper, in the first stage of the experiment, must have attracted part of the oxygen of the oxide of the blue solution; and the oxide in combination with the ammonia, being thus brought to a low state of oxidation, formed the colourless solution: on the exposure of this to the air, the oxide dissolved attracts a portion of oxygen, and the blue colour is re-produced. The compound of ammonia and oxide of copper, it has been affirmed, may be obtained in a crystallized form. These crystals, however, are rather a triple salt, obtained either by the slow evaporation of the liquor, formed by adding ammonia in excess to sulphate of copper, or by adding to it alkohol, by which minute crystals are precipitated. A combination of this kind is used in medicine, under the name of Ammoniuret of Copper. It is prepared by triturating two parts of sulphate of copper with three parts of carbonate of ammonia: an effervescence takes place from the disengagement of the carbonic acid: the mass becomes soft and humid, and when dried forms a crystalline powder of a deep violet colour. It is a triple compound of oxide of copper, ammonia, and sulphuric acid. When muriate of ammonia is digested on copper-filings, with the access of atmospheric air, the copper is oxidated, and a triple compound of oxide, ammonia, and muriatic acid, is formed. A pigment is thus prepared, named Brunswick Green.

The fixed alkalis exert less action on copper or its oxides. Their solution digested on copper-filings, has been said to acquire a blue tinge; but this is doubtful: and Vauquelin found, that perfect oxide of copper is not dissolved in perceptible quantity by potash,—a property on which he founded a method of analysing brass, to be afterwards explained. Carbonate of potash dissolves oxide of copper, forming with it a ternary combination.

Copper has been generally stated not to form any combination with carbon. Priestley had observed, however, that in passing the vapour of alkohol through a copper tube, at ignition, a substance is formed, black and friable, which he named Charcoal of Copper. This has been investigated by Van Marum. He put copper wire in an earthen tube, which was raised to a red heat, while the vapour of alkohol passed over it; carburetted hydrogen gas was disengaged, and the copper-wire was incrusted with a black matter. And in a second experiment, by passing a larger quantity of alkohol in vapour through the tube, the whole of the copper-wire that had been at a red heat was converted into a similar matter, 1049 grains being obtained from 748 grains of copper. This matter Van Marum found to be inflammable: it burnt vividly in oxygen gas, affording carbonic acid: the residual matter was partly oxide of copper, partly charcoal. These experiments apparently prove this substance to be Carburet of copper *.

Copper combines with sulphur by fusion. If three parts of copper-filings, with one of sulphur, be heated in a glass-matrass, as soon as the sulphur is in fusion, their combination commences, and is attended with a rich glow of red light. The sulphuret of copper which is formed, is of a dark colour, sometimes variegated, with a degree of metallic lustre, and exhibiting a crystalline structure: it is brittle, and more fusible than the metal. Its properties vary a little, according to the proportion of sulphur. The combination may likewise be effected by stratifying thin copper plates with sulphur in powder, and applying a gradual heat.

Sulphuret of potash combines with copper, either by fusion, or by boiling its solution on copper-filings. Sulphuretted hydrogen, and the hydro-sulphurets, throw down a precipitate of a dark brown or black colour from the salts of copper.

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* Annales de Chimie, tom. xxx. p. 322-8.

Copper can be combined with phosphorus with facility. Margraaf effected the combination by exposing to heat oxide of copper with phosphorus; but the process of Pelletier, that of heating in a crucible equal parts of copper and of phosphoric acid, with $\frac{1}{16}$ of powder of charcoal, succeeds better. This phosphuret is of a white colour, with a shade of grey, and a metallic lustre, which is impaired by exposure to the air, passing at length to a black colour. By projecting phosphorus on copper in fusion, Pelletier obtained a phosphuret of a very white colour, and a great degree of hardness. The copper had increased in weight 15 parts in 100 *. Sage, by exposing to heat two parts of phosphoric acid, with one of copper, and a twelfth of charcoal, obtained a phosphuret in which the copper had increased one-twelfth of its weight. It was of a grey colour, with much brilliancy: susceptible of a fine polish; and of the hardness of steel. It did not lose its lustre from exposure to the air, nor suffer any change for a number of years †. These phosphurets are more fusible than the metal. Exposed to a continued heat, a great part of the phosphorus is volatilized and burnt at the surface.

Copper combines with the greater number of the metals by fusion, and some of its alloys are of considerable value. It has been already stated, that alloyed with gold, it rather deepens than impairs the colour: and if pure, and not in too large a quantity, it does not much lessen the ductility, while it gives greater hardness. The specific gravity of the compound is greater than the mean of that of the two metals. Standard gold is an alloy of one part of copper in twelve in the mass. With silver it also unites with facility: in this case the specific gravity is less than the mean, or there is an expansion from the combination instead of condensation, probably from the crystalline arrangement

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* Memoires de Chimie, tom. i. p. 274. tom. ii. p. 52.

† Nicholson's Journal, vol. ix. p. 267.

which the particles of the alloy assume. A greater degree of hardness is acquired. The colour of the silver is not much altered, when the proportion of the copper is not large. The standard silver of this country contains one of copper in sixteen of the mass. Copper, fused with platina, combines with it. When the proportion of platina does not exceed one part in four or five of the compound, the alloy is ductile, of a close grain, and susceptible of a fine polish, while its lustre is not liable to tarnish. A compound of this kind, with the addition of a little arsenic to render it more fusible, has been used for constructing the mirrors of reflecting telescopes. With quicksilver, copper in thin leaves amalgamates by trituration; and quicksilver applied to the surface of copper, instantly whitens it, and, kept applied, renders it brittle. The other alloys of copper are to be afterwards noticed. With zinc it forms brass and pinchbeck; with tin, bell-metal and bronze.

Copper, besides being used extensively under the form of its alloys, is in its pure form applied to many useful purposes, as it is ductile and easily wrought. It is formed into thin sheets by being heated strongly in a furnace, and subjected to pressure under steel rollers. These sheets being light and ductile, are applied to a number of uses, as to the sheathing the bottoms of ships, &c. and to the covering the roofs of buildings. For this last purpose it is not well adapted, as it is so highly sonorous, and also from its expansibility and rigidity becomes elevated and unequal, from the effect of heat. For sheathing the bottom of ships it is preferable to every metal, as it can be made to adhere better, is less liable to wear, and prevents more effectually the adherence of marine animals. It is used in the construction of stills and boilers. It is also fabricated into a variety of household utensils, the use of which, however, for preparing or preserving articles of food, is far from being free from danger, since copper is liable to oxidation by atmospheric air, when moisture is present, and any substance, even in a slight state of acidity, acts on it still more quickly. From this cause fatal accidents have often arisen from the impregnation communicated to liquors from copper vessels. The danger has been attempted to be obviated by tinning the copper, but the tin is liable to be eroded, and this may prove more dangerous from a slight erosion not being perceived, and less care being taken, on the supposition that the copper is covered by the tin. It has been proposed to apply a covering of platina, by applying to the surface of the copper an amalgam of platina, and exposing it to the heat of ignition, repeating the operation a second time, to render the coating more perfect [*]. This would be less liable to erosion. Several of the combinations of this metal are used as paints, and some of its preparations are employed in medicine.

CHAP. X.

IRON.

This well-known metal, the most valuable of the whole class, is more abundantly diffused through nature than any other. It is found in the mineral kingdom in numerous combinations; there are even few fossils entirely free from it. It is contained in a number of vegetable products, and is obtained from their ashes when they are burnt: and it is a constituent principle of the blood, and of several animal fluids and solids. It is the principal ingredient, too, of those masses which occasionally fall from the atmosphere, the meteoric stones, as they have

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[*] Nicholson's Journal, vol. xi. p. 305.

been named. In the mineral kingdom, it is principally mineralized by oxygen, forming a very extensive family of ores, in which the oxide is more or less pure, or intermixed with other substances. In other ores it is combined with carbonic, phosphoric, and arsénic acids; and with sulphur, it forms the mineral denominated pyrites. The ores which are wrought to extract the metal, are the different varieties of the oxides. The process varies, as carried on in different countries, and as adapted to different ores; but the following is the general outline of it, especially as it is conducted in this country, on the hæmatite, and the different varieties of clay iron stone, the ores which with us are principally wrought.

The ore is roasted with a strong heat, to expel the carbonic acid, any sulphur, or other volatile matter that may be present. It is then put into a furnace of a conical form, with charcoal, or coal coaked, and is exposed to a heat, excited to sufficient intensity by a blast of compressed air urged through the furnace. A quantity of lime is also added to the ore and fuel; the advantage of which appears to be, that in combination with the argillaceous and siliceous earths, so generally contained in the iron ores, it acts as a flux to vitrify the scoriæ, and facilitate the separation of the melted metal. The proportions are various, according to the nature of the ore. The quantity of lime is about as 1 to 4, or 5 by weight of the coaked coal, that of ore about 3½, but the proportion of ore must be varied according to its richness, and according to the substances with which the oxide of iron is mixed in it. Hence different ores of iron are generally mixed together, the object being to obtain such a mixture of ores, and of other materials, as shall at least expence be sufficiently fusible, to allow of the metal being reduced and run out, and of the scoriæ being sufficiently fluid to admit of this, while at the same time the sides of the furnace shall be least acted on. Such intermixtures of ores, too, are often necessary to afford crude iron of particular qualities for purposes to which it is applied. When the furnace is once charged, the charge is renewed at the upper part as the materials sink, and the process is carried on without interruption. The slag or scoriæ is drawn off by an opening towards the bottom of the furnace. There is a cavity at the bottom, in which the melted metal is collected, and from which, as it accumulates, it runs off into moulds *.

The metal thus obtained is named Pig Iron, Crude or Cast Iron. It is far from being pure; it contains always carbon and oxygen, the former being derived from the fuel, the latter being partly a portion of what was originally combined with the metal, and partly perhaps derived from the strong blast of compressed air driven through the contents of the furnace, and necessarily presented to the metal as it is reduced and fused. Other substances are also often present, particularly phosphorus, chrome, manganese, silica, and alumina; all of which Vauquelin has shewn to exist in crude iron, and some of them also in bar iron †. Some of these may be in combination with the iron, or mechanically mixed. The oxygen, carbon, and phosphorus, there appears some reason to believe, exist in the state of oxide, carburet, and phosphuret of iron, combined with the mass of iron. The following analysis of two kinds of crude iron under the inspection of the French

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* Account of the manufacture of iron by Mr Collier, Manchester Memoirs, vol. ii.; and by Mr Muschet, Philosophical Magazine, vol. ii. A full account, too, of the process for extracting and working iron, is given in Aikin's Chemical Dictionary, under the history of this metal. And some important observations by the French metallurgists, accompanied with analysis of the ores operated on, and of the scoriæ after their fusion, are given in the Journal des Mines, of which there are abstracts in the 5th and 6th volumes of the Retrospect of Discoveries.

† Nicholson's Journal, vol. xxi. p. 59.

Board of mines, appear to have been executed with much accuracy. The first gave 93.15 of iron, 3.5 of silica, 2.1 of charcoal, 0.8 of alumina, 0.75 of phosphorus, 0.5 of lime, and 0.3 of sulphur, with a trace of manganese, but none of chrome. The other gave 96.79 of iron, 2.4 of charcoal, 0.54 of silica, 0.27 of phosphorus, and a little chrome and alumina, but no trace of sulphur. The scoriæ from iron ores consist principally of silica, lime, and alumina, with a portion of oxide of iron, and smaller quantities of manganese, chrome, and magnesia. It is not improbable that the metallic bases of these earths exist combined with the iron, rather than the earths themselves, and that they are afforded in the latter state, in consequence of oxidation during the analysis.

From the presence of these foreign substances, the qualities of cast iron are various. Three kinds of it have been distinguished, which pass into each other,—the white, the grey, and the black. The first named White Crude Iron, is of a white colour, which is displayed in a fresh fracture: the fracture exhibits also an appearance of striæ, or indistinct crystallization; and its surface is oxidated: it is extremely brittle: it is supposed to derive its qualities from a portion of oxygen, or rather perhaps of oxide of iron. The second, the Grey Crude Iron of Commerce, is of a light grey colour: its fracture is granulated and dull; and it is less brittle than the former: it is supposed to contain both oxygen and carbon. There is, lastly, the Black Crude Iron, the fracture of which gives a dark grey colour, inclining to blue, and presents granular concretions. This is supposed to contain principally carbon or carburet of iron combined with the metal: it is softer, and also more fusible, than the others. The production of these varieties depends principally on the proportion of carbonaceous matter employed in the reduction, relative to that of the ore; hence much of the difference in their qualities probably depends on the proportion of carbon retained by the iron; and accordingly, from all these varieties of iron, carbon is extracted by analysis. Peculiar properties must also, however, be communicated by the other ingredients; and accordingly, they depend partly on the kind of ore, so that a considerable degree of practical skill is required in assorting the different ores. Much also depends on the management of the blast of compressed air.

Iron in any of these states is much more fusible than when pure; hence it is capable of being melted, and cast into moulds, so as to form vessels of any form. It is also, however, much more brittle and hard, so much so, that it cannot be flattened under the hammer; it is therefore unfit for many purposes to which pure or malleable iron is from its tenacity and softness adapted.

To obtain pure iron, in other words, to free crude iron from the oxygen, carbon, and other foreign substances contained in it, it is subjected to two operations,—melting and forging. The fusion is performed in a furnace. The melted metal is either run out to free it from the scoriæ which have separated, and is repeatedly subjected to this, until it attain a degree of malleability, when it is submitted to the action of the forge hammer: Or the metal is kept in fusion in a furnace, and while liquid is stirred frequently, to facilitate the combination of the carbon and oxygen: a lambent blue flame at length appears on its surface, probably from the formation and disengagement of carbonic oxide. After some time its fluidity diminishes, and it assumes the consistence of a stiff paste. It is then subjected to the action of a very large hammer, or to the more equable, though less forcible, pressure of steel rollers, by which a portion of oxide of iron, and other heterogeneous substances not consumed during the fusion, are forced out. The iron in this state is no longer granular in its texture: it is soft, ductile, and malleable, and much less fusible. It is then named Forged Iron, or Bar Iron. A considerable loss of weight attends the process, partly from the dissipation of the foreign substances, partly from the oxidation which the iron suffers. Vauquelin examined the sublimed matter collected in the chimneys of the refining furnace; he found, that in this sublimed iron are present oxide of manganese, silex, phosphoric acid, and a great deal of chrome; and in the scoriæ he discovered the same substances, with alumina and lime *.

Forged iron is not uniform in its qualities, but appears under different varieties. Pure iron is distinguished by its very difficult fusibility, its softening when heated, so that two pieces can be joined together, and its great ductility and malleability. There is one kind of forged iron, which, when cold, has the ductility of the pure metal, and is even soft; but when heated, it is so fusible and brittle, that it is incapable of withstanding the stroke of a hammer. This is termed Hot Short iron. There is another variety possessed of the opposite property: it sustains the most violent heat without exhibiting any sign of fusion: while hot it is highly ductile, and may therefore be extended under the hammer; but when cold it is extremely brittle, even more so than crude iron. This has been named Cold Short Iron.

The causes of these peculiarities have not been fully discovered. Bergman discovered that a white powder is deposited from cold short iron during its solution in acids, which, by reduction with charcoal, assumed a metallic appearance. This he regarded as a peculiar metal, to which he gave the name of Siderite, and supposed it to be the cause of the cold short property. It was afterwards discovered to be phosphuret of iron. Added to malleable iron, it communicates this peculiar property; and those ores which produce this kind of iron, are said to be those in which traces of phosphoric acid can be discovered. It has also been affirmed, however, that every kind of malleable iron may, by peculiarities in the management of the refining process, be made to afford cold short iron, and that the

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* Nicholson's Journal, vol. xxi. p. 32.

quality arises from some peculiar combination of oxygen with the metal. Still less is known with certainty with regard to the nature of hot short iron. The peculiar property belonging to it has been ascribed to the presence of carbon, sulphur, or sulphurous acid, copper, or arsenic, and also, according to Vauquelin, of manganese and chrome.

Forged iron, free from these peculiarities, or the metal in its pure state, is malleable and ductile, and is extremely infusible.

There is one other state in which it exists, that of Steel, distinguished by the extreme hardness and elasticity which it can acquire. This is a compound of iron with carbon, and is to be noticed as such.

The colour of this metal is a light grey, with a shade of blue: its texture is fibrous; its fracture is brilliant and fine grained: its mean specific gravity is 7.700. Its hardness is superior to that of the other metals: it is very malleable, and exceedingly ductile, so that a finer wire can be drawn from it than from any metal: a wire 0.078 of an inch in diameter, supports 549 libs. It is highly elastic. By mere hammering it may be brought to ignition, from the quantity of caloric rendered sensible.

Iron is peculiarly distinguished by its magnetic property: it is attracted by the magnet, and it acquires the power of magnetism, by friction, by being suspended in a perpendicular direction, by the action of electricity, and of various other causes. It has been supposed, that it is the only substance which possesses this singular property; since, in whatever other metal or fossil it has been observed, iron, it is alledged, has been detected; and, in proportion as the iron is abstracted, the magnetic power is diminished. It appears, however, that nickel, and probably also cobalt, are magnetic metals. The magnetic quality of iron is lost in some of its combinations, while it remains in others. It continues, though the metal be oxidated, until the quantity of oxygen exceed 20 parts with

80 of iron, and, according to the experiments of Darso, remains when the metal is in a higher state of oxidation, if the oxide is in a certain state of aggregation, or its particles are much approximated *. Mr Lane has shewn that the smallest quantity of inflammable matter, brought into combination with oxide of iron by heat, increases, and in some cases developes its magnetic power; and he has even concluded, that pure oxides of iron, free from inflammable matter, are not magnetic †. Carbon enables iron to retain the magnetic influence, as is exemplified in steel. When combined with sulphur to a certain extent, that of 36 with 64 of iron, the compound has a strong magnetic polarity, and retains this power, so that the mass acts as a permanent magnet, as Mr Hatchet ascertained ‡: combined with 45 or 46 parts, it is capable, he found, of being attracted by the magnet; but, when combined with 52 or more, it does not affect the magnetic needle. Phosphorus, Mr Hatchet found on experiment, had the same effect; rendering iron a powerful and permanent magnet. The three inflammables thus exert a similar action on iron with regard to this property.

Pure iron is extremely infusible. When in contact with burning fuel, it fuses indeed without great difficulty, because it attracts a portion of carbon and oxygen, by which its fusibility is increased. But in covered vessels, it can scarcely be melted in any furnace. This, however, has been accomplished. Mr Wedgwood fused soft iron nails in a Hessian crucible in an air furnace, at a heat equal to 154 of his scale. Sir George Mackenzie found, that small pieces of soft iron were fused in a covered crucible, when the temperature indicated by one of the pyrometrical pieces of Wedgwood was 158°. In a furnace, in

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* Nicholson's Journal, vol. xvii. p. 350.

† Philosophical Transactions, 1805.

‡ Ibid. 1804, p. 335.

which the temperature was 153, the same iron did not melt. Its melting point must therefore be near 158 of Wedgwood *. Cast iron was found by Mr Wedgwood to melt at 130, but not at 125 †.

At a temperature far below that necessary for its fusion, iron softens, so that its surface appears as if it were covered with a thick tenacious fluid: this softness extends through the whole mass. In this state the iron is malleable; hence it can be beaten into any shape; and if two pieces thus softened be hammered together, they unite as firmly as if they had been fused into one mass. This property, named Welding, belongs to no other metal but platina, and to it in a very inferior degree. It is a very valuable one, as by means of it malleable iron may be worked into various forms, and applied to purposes for which it could not otherwise be used. The temperature at which this softening or welding of iron takes place, is a full white heat. Mr Wedgwood has stated it from 90 to 95 of his scale; but this is undoubtedly too high. From some facts related by Sir James Hall, it appears, that at certain temperatures, superior to the welding temperatures, all iron falls to pieces under the hammer, and that this happens at different temperatures, in the different varieties of the iron of commerce,—in cast iron at about 15° of Wedgwood, in steel at 30°, in Swedish iron at 50° or 60°, and in Siberian iron at 100° ‡.

Iron heated under exposure to atmospheric air, suffers oxidation. If its surface has been polished, ranges of prismatic colours appear upon it, arising probably from this cause: when the temperature is raised to ignition, scales are formed, which may easily be detached; they are thus obtained in hammering a bar of ignited iron on the anvil.

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* Nicholson's Journal, 4to, vol. iv. p. 109.

† Philosophical Transactions, vol. lxxii. p. 519.

‡ Edinburgh Philosophical Transactions, vol. vi.

The sparks struck by flint from steel are similar. When iron-wire is introduced at the temperature of ignition into oxygen gas, it burns with vivid coruscations, and affords the same oxide, which is fused into globules by the intense heat. This is the Black Oxide of iron. It is brittle, and easily reduced by trituration to a powder, which is of a black colour. It is attracted by the magnet. The metal is supposed to exist in it in the first degree of oxidation. By exposing this oxide to a continued heat, stirring it under exposure to the air, it changes its colour, and becomes red, from a higher degree of oxidation, losing at the same time the property of magnetism. This forms the Red Oxide. These oxides can be obtained by other processes. The black oxide is formed by keeping iron-filings immersed under water, or by passing the vapour of water over ignited iron; and it exists in some of the saline combinations of the metal, from which it may be precipitated by an alkali; a light green precipitate being afforded, which, exposed to a moderate heat in close vessels, becomes black. The red oxide is obtained, by a similar process, from those saline combinations in which the metal is at a high state of oxidation, from the nitrate, for example, decomposed by ammonia, the precipitate being washed, dried, and calcined at a red heat.

Some uncertainty exists, however, with regard to the oxides of iron. Proust advanced the opinion, that this metal, in common with others, is susceptible of only two degrees of oxidation, those forming the black and the red oxides. In the first, the proportion of oxygen had been inferred by Lavoisier to be 27 of oxygen to 100 of iron; according to Proust, it is 28. In the second, Proust stated the proportion of oxygen at 48 *. Other chemists, in the farther prosecution of the subject, gave similar proportions, but with some variations. According to Bucholz,

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* Annales de Chimie, tom. xxiii. p. 85.

the proportion of oxygen in the black oxide is 30 to 100, in the red 42 [*]. According to Hassenfratz, they are 30 of oxygen in the one, and in the other 45 [†]. And Dr Thomson, admitting the estimate in the latter, stated the proportion of oxygen in the former at 27.5 [‡]. More recently Berzelius has investigated it with much care, and has fixed the proportions in the black oxide at 29.5 of oxygen, and in the red at 44.25, to 100 of iron [||]. Dr Wollaston adopts very nearly the same proportions, 29 in the one, and 43.5 in the other.

The existence of some other oxides of iron has been inferred. Chenevix observed, that if a muriate of iron be formed by boiling muriatic acid on a larger quantity of metal than it can dissolve, a solution is obtained which is colourless, and which, when decomposed by an alkali, affords a white precipitate. This he regarded as an oxide in a lower degree of oxidation than the black [§]. And Thenard had pointed out the white precipitate which is thrown down from green sulphate of iron by an alkali, and which he affirmed retains no sulphuric acid, as an oxide distinct from the black or red, and probably at a lower degree of oxidation than the former. And these three oxides he supposed to exist in various saline combinations of the metal [¶]. These conclusions, however, are not established. Bucholz found that the white oxide of Thenard is a sub-sulphate, which was confirmed by Dr Thomson; and Berzelius found that from the muriatic solution to be a hydrate.

Gay Lussac affirmed, that an oxide is formed by passing the vapour of water over iron in a tube at the tempe-

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[*] Nicholson's Journal, vol. xxv. p. 553.

[†] Ibid. vol. xxvi. xxviii.

[‡] Ibid. vol. xxvii.

[||] Philosophical Magazine, vol. xli. p. 535.

[§] Philosophical Transactions, 1801, p. 225.

[¶] Nicholson's Journal, vol. xiv. p. 224.

rature of ignition, which is at an intermediate degree of oxidation between the black and the red, containing 37.8 of oxygen, with 100 of metal *. There appear also to be several oxides of iron distinct from each other as species in the mineral kingdom. Hauy has pointed out three very different in their crystalline forms and essential characters: Bournon has added a fourth; and Daubisson increases the number even to seven. These facts have been accounted for by supposing, that such oxides are compounds of the black and of the red. Berzelius has in particular maintained this opinion with regard to the oxide pointed out by Gay Lussac, and to some of the native oxides, and has stated some facts, to shew the facility with which they can be resolved into these two oxides †. But it may be doubted if they are altogether conclusive.

The proportions of oxygen in the black and red oxides present one of those anomalies which have occurred in the law of definite proportions,—that the larger proportion of an element in a combination is not a simple multiple of the other proportion in which it combines with the same base, for the proportion 43.5 in the red, to that of 29 in the black, is not that of 2 to 1, but of $1\frac{1}{2}$ to 1. This has been sought to be removed, by supposing that a lower degree of oxidation exists, in which 100 of iron are combined with 14.5 of oxygen: the series would then be 1, 2, 3. But the existence of this oxide is not established; and besides, from the equivalent number of the black oxide, as inferred from its saline compounds, it must be inferred to be a protoxide, which precludes this solution of the difficulty. On the atomic hypothesis it has been attempted to be obviated, by considering the black oxide as com-

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* Annales de Chimie, tom. lxxx. p. 163. Annales de Chimie et Physique, tom. i. p. 33.

† Annales de Chimie et Physique, tom. v. p. 150. Annals of Philosophy, vol. iii. p. 357.

posed of 1 atom of iron with 1 of oxygen, and the red of 2 atoms of iron with 3 of oxygen, an opinion which, if it is not a mere verbal distinction, would present an anomaly as great as that which it is intended to remove.

The oxides of iron cannot be reduced by exposure to heat alone; but when mixed with carbonaceous matter, and raised to the necessary temperature, the oxygen is abstracted, and the iron returns to the metallic state, combining at the same time with a portion of carbon.

Iron suffers oxidation, at a low temperature, when exposed to a humid atmosphere. This is the rusting of iron. The oxygen appears to be derived from the water, as, when the experiment is performed with moistened iron-filings, hydrogen gas is evolved, carbonic acid is also absorbed, and perhaps also formed by the oxidation of the portion of carbon which iron generally contains. The rust of iron is a carbonate, or rather a sub-carbonate. When water is decomposed by iron, without the access of air, either at a low, or at a high temperature, it is a pure oxide that is obtained.

Iron is oxidated and dissolved by the acids, and in these combinations the metal exists, combined with different proportions of oxygen, forming therefore with the same acid, salts with different properties. When neutral they are in general soluble and crystallizable: they have an astringent taste. When the oxide is at a high degree of oxidation, they afford a rich blue precipitate with an alkaline prussiate, and a deep purple one with infusion of galls; two re-agents which form very delicate tests for discovering this metal.

Sulphate of iron has long been known, and in use in the arts, under the name of Green Vitriol. It is usually prepared from the decomposition of the native sulphuret of iron, by exposure to air and humidity, oxygen being absorbed, the iron being oxidated, and the sulphur converted into sulphuric acid, with which the oxide combines. The salt is extracted by lixiviation and crystallization, but it is not so pure as when formed by the solution of malleable iron in sulphuric acid. The acid, when in its concentrated state, and in the cold, scarcely exerts any action on the metal: if heat be employed, it is decomposed, sulphurous acid gas is disengaged, and sulphate of iron formed. If it be diluted with four or five parts of water, the solution proceeds rapidly in the cold: the acid, by a resulting affinity, enables the iron to attract oxygen from the water, hydrogen gas is disengaged, and the oxide of iron combines with the sulphuric acid. The solution is of a pale green colour, and, by evaporation, affords crystals, which are of a lively green. This salt, in its crystallized state, consists, according to Kirwan, of 28 parts oxide of iron, 26 of sulphuric acid, 8 of water of composition, and 38 of water of crystallization: according to Berzelius, of 25.7 of oxide, 28.9 of acid, and 45.4 of water: or excluding the water, of 100 of acid with 88 of the black oxide of iron.

The form of its crystals is a rhomboidal prism. They are soluble in six parts of cold water. Exposed to heat, they suffer the watery fusion. When the water is dissipated, the salt remains in the state of a greenish-white mass: by increasing the heat, it suffers decomposition, the sulphuric acid is expelled, and this constituted the old process by which this acid was obtained; at the same time a part of the acid is decomposed: the black oxide of iron, which is the base of the green sulphate, receives part of its oxygen, so as to pass to the state of red oxide; sulphurous acid is disengaged; and this being absorbed by the sulphuric acid, which is the product of the distillation, renders it concrete, and gives it the property of emitting fumes when exposed to the air. This is the explanation which used to be received, but it is doubtful; and the Glacial Oil of Vitriol, as this substance has been named, has been considered as real sulphuric acid. The red oxide which remains, received the name of Colcothar of Vitriol.

Sulphate of iron becomes opaque when exposed to the air: its colour becomes yellowish; and its surface is at length covered with a powder of this colour. This change is owing not merely to the abstraction of its water of crystallization, but to the absorption of oxygen, in consequence of which the metal passes to a higher state of oxidation. Hence the same change goes on in its watery solution. This is at first of a pale green colour, and transparent; but on exposure to the atmosphere, it becomes turbid; and a yellowish precipitate subsides. This is owing to the absorption of oxygen; and the metal, as it thus becomes more highly oxidated, requiring more acid for its saturation, in conformity to the law observed in the relation of metallic oxides to acids, there is not a sufficient quantity of acid present to retain the more perfect oxide in solution; hence it is precipitated, probably in the state of a sub-sulphate.

Besides the green sulphate of iron, therefore, the base of which is the black oxide, there is a different compound in which the metal is in a higher state of oxidation. This has been named the Red Sulphate. It is obtained by leaving the liquor, which remains after the crystallization of the green sulphate, exposed to the atmosphere: the oxide of the salt in solution continues to absorb oxygen: and as there is usually an excess of acid in the liquor, it saturates this more perfect oxide as it is formed. It is obtained in a more perfect state by heating the solution of the green sulphate with nitric acid, while any nitric oxide gas continues to be disengaged. It consists, according to Berzelius, of 60.44 of sulphuric acid, and 39.56 of oxide of iron; or 100 with 65.5.

The green and the red sulphates of iron have one chemical property by which they can be discriminated, and, if in a state of intermixture, be separated. The green sulphate is not soluble in alkohol, while the red is easily dissolved. The red sulphate is also more abundantly soluble in water, and cannot be crystallized. When its solution is evaporated, it forms a mass of a yellowish red colour, which is deliquescent. Substances capable of abstracting the oxygen of its oxide partially, as sulphurous acid, or sulphuretted hydrogen, bring it back to the state of the green sulphate. Iron-filings digested with it, produce the same change *.

The essential difference between these two salts is conspicuous in the phenomena presented by the action of reagents upon them. The green sulphate of iron, decomposed by soda or potash, gives a precipitate of a green colour; by ammonia, one of the same colour, but deeper: both become black when dried in close vessels. The red sulphate gives, on the other hand, precipitates of a yellow colour, approaching to red, and retaining this redness when dried. The green sulphate gives a white precipitate with prussiate of potash; the red sulphate, one which is of a rich blue colour: the former is not altered by infusion of galls, the latter acquires a deep purple colour. From the solution of the green sulphate, sulphuretted hydrogen produces no precipitate: from that of the red sulphate it throws down a dark precipitate.

The tendency of the oxide of iron in the green sulphate to pass into a higher degree of oxidation is such, that it is difficult to obtain these phenomena in perfection. Thus, though tincture of galls does not at first alter the colour of its solution, yet, in a few moments, exposure to the atmosphere is sufficient to communicate a violet tint; and though the prussiate of potash gives a white precipitate, this, from the same cause, rapidly assumes a bluish appearance. It is even difficult to obtain it in such a state as not to be coloured by infusion of galls, or to give a precipitate of a light blue, with prussiate of potash. It is procured at the *minimum* of oxidation, by digesting iron-filings with

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* Nicholson's Journal, 4to, vol. i. p. 455.

the solution of the common sulphate, by transmitting through the solution sulphuretted hydrogen gas, or by dissolving the artificial sulphuret of iron in diluted sulphuric acid; the sulphuretted hydrogen, which rises through the liquid as the solution proceeds, preserving the metal at the lowest degree of oxidation, and any excess of it being expelled by boiling for a few minutes: it then gives a white precipitate with the alkaline prussiate, and does not alter the colour of infusion of galls. These differences of colour have usually been ascribed to the formation of different compounds, by the union of these re-agents with the different oxides of iron; but they are probably as much owing, as Berthollet suggested, to the iron in these different states of oxidation exerting different forces of affinity to the acid: its affinity in the low state of oxidation being too strong to admit of it being precipitated, while in the higher degree of oxidation the affinity is weaker. Hence, if the affinity of the acid be weakened by dilution with water, or by an alkali, the dark colour is produced even with the salt, containing the iron at the *minimum* of oxidation.

Proust supposed, that the two sulphates of iron are of determinate oxidation, and that any salt or solution, which, from the phenomena it presents with re-agents, appears to be intermediate between them, derives this from an intermixture of the one with the other *. This is rather hypothetical. The surface of the crystals may, from the action of the air, become more highly oxidated than the internal part. But, in the solution, the separate existence of the two salts can scarcely be supposed: the one at the lower state of oxidation will share the excess of the oxygen of the other, and one uniform intermediate combination be established. The oxide in this intermediate state, it may be presumed, *a priori*, from the law which regulates metallic solutions, will have a relation to the acid different

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* Nicholson's Journal, 4to, vol. i. p. 454.

from the mean of the two oxides: it may require, for example, more acid to hold it in solution, than the two salts contained; a precipitate will then be formed. And accordingly Berthollet found, that a precipitate is soon formed, on mixing solutions of the salt at the *minimum* and the *maximum* of oxidation. He adds, what appears to be just, that a division of the oxygen of the salt in solution may happen even in the course of its crystallization; the crystals which are formed in successive crystallizations of sulphate of iron, are of different shades of colour, being pale at first, and becoming more and more green, until the uncrystallizable liquid remains nearly in the state of the red sulphate *.

The property which green sulphate of iron has of absorbing nitric oxide gas, and the application of this to eudiometry, has been noticed under the history of that gas.

Sulphate of iron is of extensive use in some of the arts, particularly in the art of dyeing, as forming, by its action on vegetable astringents, the basis of black dyes; and also in the formation of some pigments, as that of the prussian blue of commerce. For these purposes, it requires to be in the state of the red sulphate; but in using it this is of inferior importance, since in these combinations the iron quickly passes from a low to a high state of oxidation, from the action of the atmospheric air.

Sulphurous acid, combined with water, acts on iron-filings: a little hydrogen gas is at first disengaged, which soon ceases: the liquor becomes brown, and ultimately green. This solution, when acids are added to it, effervesces from the extrication of sulphurous acid, and a portion of sulphur is deposited. It appears, therefore, that in the action of sulphurous acid on iron, part of the acid is decomposed, its oxygen being attracted by the metal, and forming an oxide, with which another portion of the

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* Chemical Statics, vol. ii. p. 350.

acid combines, while the sulphur of the portion of decomposed acid enters also into the combination. The solution, therefore, is not that of a pure sulphite, but of a sulphuretted sulphite. The pure sulphite may be obtained, by dissolving oxide of iron in sulphurous acid: it is soluble in water, insoluble in alkohol; gives a green precipitate with the alkalis; is not coloured by infusion of galls or the prussiates; absorbs oxygen on exposure to the air, so as to pass to the state of sulphate; and yields sulphurous acid from the affusion of other acids. The sulphuretted sulphite is soluble in alkohol, and is permanent in the air.

Nitric acid acts on iron forcibly, is decomposed, and nitric and nitrous oxide gases, mingled with nitrous acid vapour, are rapidly disengaged; the iron passing to a high state of oxidation, and retaining a portion of the acid in combination, but not sufficient to form a soluble compound. When the acid is largely diluted with water, the action is more moderate, and the iron is slowly dissolved. The solution is of a colour varying from yellowish brown to green. It cannot be evaporated so as to afford crystals, the heat necessary causing the farther decomposition of the acid; and the iron, passing to a higher state of oxidation, is in part precipitated in the state of a sub-nitrate. On exposing it to the air, a similar change is effected, oxygen being absorbed. Even in any state, the nitrate of iron does not appear to be obtained, with the metal, at the *minimum* of oxidation; as from its solution, prepared with diluted acid and in the cold, the alkalis throw down a yellowish or brown precipitate. Nitrate of iron is decomposed by heat, and the metal remains highly oxidated, in a powder of a bright red colour.

Iron is dissolved with facility by muriatic acid, even when it is diluted with three or four parts of water: the iron is oxidated by decomposing the water; and hence the solution is accompanied with the disengagement of hydrogen. It may be either at the *minimum* or the *maximum* of oxidation, according to the manner in which it has been effected. It exists nearly in the former state, when iron-filings are dissolved in diluted muriatic acid, and the atmospheric air is excluded from the solution; or more perfectly so, when the artificial sulphuret of iron is dissolved in the acid, applying to the solution a moderate heat, so as to expel any sulphuretted hydrogen gas. The solution is of a yellowish green colour, and by evaporation affords crystals, the colour of which is a pale green. When it is exposed to the air, oxygen is absorbed, the iron passes to a higher state of oxidation, and is in part precipitated in the state of a sub-muriate. The green muriate of iron, as the salt at the low degree of oxidation may be named, is acted on by re-agents nearly in the same manner as the green sulphate. It is decomposed by the alkalis, giving a green precipitate: its colour is not altered by infusion of galls; and with the alkaline prussiates it forms the white prussiate of iron. Its solution absorbs nitric oxide gas with even more facility than the solution of the green sulphate, and this impregnated solution absorbs oxygen, and suffers changes similar to those of the sulphate, already described.

The muriate in which the metal is at a higher state of oxidation, may be formed by dissolving the red oxide in muriatic acid: the solution is of a yellow colour, more or less deep, according to its state of concentration. It does not crystallize, but by evaporation affords a yellow deliquescent mass. It is soluble in alkohol, the solution being of a lively yellow colour, and forming a tincture which is used in medicine. Decomposed by heat, or by concentrated sulphuric acid, it gives out muriatic and oxymuriatic acids. By continuing the application of heat, a muriate of iron is sublimed. Decomposed by the alkalis, it gives a yellowish brown precipitate.

In oxymuriatic gas, iron burns when it is gently heated, and a product is obtained analogous to the muriate at the *maximum* of oxidation, in a concentrated state. It is very volatile, and condenses in crystalline scales, of a fine yellow colour, with much lustre. Considering it as a chloride, it is composed, according to Dr J. Davy's analysis of it, of 35.1 of iron, and 64.9 of chlorine. The green muriate evaporated to dryness is, according to the same view, composed, according to his analysis of it, of 46.57 of iron, and 53.43 of chlorine.

Chloric acid, according to Vauquelin, dissolves iron rapidly, without the evolution of any gas. The colour of the solution is at first green, but soon becomes red, without the access of air: when evaporated, it forms a gelatinous mass of a deep red colour, which when dried becomes transparent, and is still soluble in water; when heated strongly, it gives out oxymuriatic gas: it precipitates nitrate of silver, and gives a red precipitate with alkalis. Infusion of galls, and prussiate of potash, produce with it a green colour.

A ternary compound of oxide of iron with muriatic acid and ammonia, is formed by mixing oxide of iron and muriate of ammonia, and applying heat to the mixture in a matrass: a yellow sublimate is obtained, which has been used in the practice of medicine.

Carbonic acid is capable of combining with oxide of iron. When water, impregnated with this acid, is kept on iron-filings in a closed phial, it acquires the styptic taste of the salts of iron, part of the iron being oxidated probably by the oxygen held in solution by the water, and this oxide combining with the acid. The common rust of iron contains a portion of carbonic acid, either absorbed from the atmosphere, or formed from the oxygenation of the carbon which iron usually contains. It is scarcely disengaged by the affusion of an acid, and does not appear to be in sufficient proportion to neutralize the oxide. A carbonate is obtained by decomposing sulphate of iron by an alkaline carbonate; the precipitate formed when the solutions of the two salts are mingled together, is of a deep green colour; but, in drying, assumes the usual colour of the rust of iron. Carbonate of iron frequently occurs in mineral waters, being held in solution by an excess of carbonic acid. This escapes when the water is exposed to the atmosphere; and the iron becomes more highly oxidated; there is a precipitation of an oxide or a sub-carbonate. This forms the yellow sediment so common in chalybeate springs.

Phosphoric acid scarcely dissolves iron. The phosphate may be obtained, by mixing solutions of sulphate of iron and phosphate of soda; a precipitate is formed, of a white colour, and insoluble in water. It is capable of being fused by a violent heat into a globule having metallic brilliancy. Heated with charcoal, the acid is reduced, and phosphuret of iron formed. Some observations on the phosphates of iron have been given by Berthier. That containing the metal at the minimum of oxidation, obtained by decomposing a saline solution of iron in that state by an alkaline phosphate, is white, but becomes grey or greenish blue, is soluble in the weaker acids, and by nitric acid is brought to a higher state of oxidation. The phosphate at the maximum of oxidation, is obtained by decomposing a solution containing the metal in that state by phosphate of ammonia; it is of a yellowish white colour and gelatinous; it is insoluble in water, or in the weak acids, but is dissolved by the stronger acids; it is decomposed by the alkalis at a boiling heat. It contains 52 of red oxide, and 48 of acid, and appears to contain an excess of oxide *. Phosphate of iron exists as a mineral production, both massive and crystallized.

Fluoric acid combined with water dissolves iron, with a disengagement of hydrogen gas. The solution does not crystallize; but, by concentration, assumes a gelatinous

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* Retrospect of Discoveries, vol. v. p. 484.

consistence. It is decomposed by heat, which expels the acid.

The action of boracic acid on iron is so weak, that scarcely any sensible portion of the metal is dissolved. The acid, in combination with oxide of iron, is obtained by adding a solution of borate of soda to a solution of sulphate of iron. The compound is insoluble.

An acid from the animal kingdom, the Prussic Acid, exerts a strong attraction to oxide of iron, in consequence of which it affords one of the re-agents of most delicacy, by which this metal can be detected in any of its combinations. When the iron is at the minimum of oxidation, the compound is white; but when more highly oxidated, it is of a rich blue colour, the latter forming the basis of Prussian Blue. These combinations are to be afterwards noticed.

Another acid from the vegetable kingdom, Gallic Acid, affords also a re-agent which detects the presence of iron. The compound it forms with oxide of iron, is of a deep purple colour. This test is usually employed under the form of infusions of the vegetable astringents, such as the gall-nut, in which case the effect depends as much on another principle, the tannin of the astringent, as on the action of the gallic acid which accompanies it. The more full account of these combinations belongs to the chemical history of these principles.

Succinic acid affords a valuable re-agent in detecting iron, and estimating its quantity; it forms with the peroxide an insoluble compound; the metal in this state is therefore precipitated from any of its saline compounds by succinate of ammonia, and the succinate of iron can be afterwards decomposed by heat. Benzoic acid produces a similar effect, but is a less delicate re-agent.

Iodine acts upon iron-filings readily when heated with them; the product is a substance of a brown colour, which melts at a red heat, dissolves in water, and gives a solution of a clear green colour.

The alkalis do not act on metallic iron, and scarcely dissolve any perceptible quantity of its oxides. The perfect oxide of iron is partially decomposed by ammonia, a portion of its oxygen being abstracted by the hydrogen of the alkali, so that it passes from the red colour to a brown or black. Fourcroy affirmed, that the same change is effected by the action of the fixed alkalis, when assisted by heat. The alkalis appear also to form ternary or quaternary combinations with the oxides of iron and several of the acids. Thus, carbonate of potash or of ammonia, added to a solution of nitrate of iron, throws down a yellowish red precipitate, which is re-dissolved when an excess of the carbonate is added.

The oxides of iron, fused with the earths, produce coloured enamels; and, in the humid way, they contribute to their concretion and induration: hence, they enter into the composition of the best cements.

Iron has a strong attraction to Carbon, as is evident from the iron combining with a portion in the process of its reduction: in this state, however, it also contains oxygen. The combination of iron with carbon alone exists in nature, forming the mineral substance known by the name of Black Lead, and described by mineralogists under the names of Plumbago and Graphite. Produced by artificial arrangement, it forms Steel.

It has been stated, under the history of carbon, that Scheele proved that Plumbago consists principally of carbonaceous matter; he farther found, that a residuum of iron was obtained in deflagrating it with nitre, or by exposing it to heat until it ceased to lose weight, the quantity amounting to about 10 parts in 100. Pelletier analysed a number of specimens of plumbago, and always detected iron in it. The plumbago from Cumberland appeared, from his experiments, to contain the smallest proportion *.

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* Mémoires de Chimie, tom. i. p. 184.

Saussure found the quantity of iron in plumbago apparently pure, to amount to about 4 parts in 100. Mess. Allen and Pepys obtained, in the combustion of plumbago, a residue from 100 parts of 5 of oxide of iron, which amounts nearly to the same proportions. Schrader obtained from the graphite of Cumberland, which is generally very pure, about 5.5 of black oxide of iron : he also found in the residue silica, alumina, and oxide of titanium, evidently foreign ingredients *.

Plumbago in its combustion, it has been already stated, was found by Mess. Allen and Pepys, to afford, from the consumption of its carbonaceous matter, the same quantity of carbonic acid as calcined charcoal. Saussure found too, that its carbonaceous matter affords no sensible portion of water in burning, nor gives any indication of containing hydrogen as charcoal does †. Davy, on submitting it to intense heat *in vacuo*, excited by a galvanic battery, found it to give out no elastic fluid, nor to suffer any evident change ‡. He has since found, as has been already stated under the history of diamond, that an appearance of vapour attends its combustion in oxygen gas, nearly as it does that of charcoal, whence the presence of hydrogen may be inferred. But if it is admitted, the quantity is extremely minute.

There is some uncertainty whether iron is essential to the constitution of plumbago. That it is so, might be inferred from its being uniformly present, for on no other supposition than that they are intimately combined, can this constant conjunction be explained. And the iron appears farther to modify the properties of the plumbago, as no other variety of carbonaceous matter has the same appearance and characters. The conclusion involves a diffi-

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* Annals of Philosophy, vol. i. p. 299.

† Nicholson's Journal, vol. xxvi. p. 300.

‡ Philosophical Transactions, 1809.

culty in the atomic theory, the proportion of iron to the carbon being so small, that from their relative combining weights, the constitution of the compound is such, as can scarcely be admitted; it being necessary to suppose, as Dr Thomson remarks*, that 1 atom of iron is combined with 24·8 atoms of carbon. But this is only an objection to the atomic hypothesis, not to the conclusion, that plumbago is a carburet of iron.

Plumbago burns very slowly, and with scarcely any flame: the residue consists of the iron, and impurities mixed with it. When thrown with a large quantity of nitre into an ignited crucible, it is rapidly oxidated. Ten parts of nitre are requisite to burn one part of plumbago, while five parts are sufficient for the deflagration of one part of charcoal. Scheele remarked, that when digested and boiled in the acids, it is not sensibly dissolved, farther than that a small portion of iron is extracted. This was confirmed by Pelletier. It is singular, that it is not altered by repeatedly distilling nitric acid from it. Sulphuric acid distilled from it, is partially decomposed and converted into sulphurous acid, as Pelletier found, no doubt from its greater fixity, whence the temperature can be raised higher. From the same cause, arsénic acid and phosphoric acid, when heated with it, are de-oxidated. The fixed alkalis, exposed to a strong heat with plumbago, were observed by Scheele to afford inflammable air; the alkali also losing its causticity, and effervescing with acids. And Pelletier obtained carbonic acid by this effervescence; the water combined with the alkali being decomposed, whence the origin of the carbonic acid and hydrogen gas. Heated with a number of the metallic oxides, it reduces them to the metallic state. Pelletier could not succeed in combining it with any of the metals.

Native carburet of iron is applied to several uses. It

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* Annals of Philosophy, vol. ii. p. 293.

forms the best kind of crayons; slips of it being cut and fixed in a groove, in a slip or cylinder of wood. It is employed in the construction of crucibles, and small furnaces; its powder being mixed with clay, baked and hardened by a strong heat. It communicates tenacity to the clay, which renders the composition less liable to be rent; and being enveloped in the clay, while its combustibility is at the same time so inconsiderable, it scarcely suffers any change in the most intense fire. It is sometimes added to the earths, of which earthen ware is prepared. When rubbed on the surface of iron which is to be exposed to humidity, it retards its rusting. It is used to give a lustre to small lead shot. And by its softness and lubricity, it is adapted to diminish the friction of machinery, and facilitate the motion of one surface over another.

Pelletier observed, that in the fusion of some ores of iron on the large scale, a substance separates, and floats on the surface, which resembles plumbago in its scaly texture, lustre, and softness. It had also the same chemical qualities, burning with difficulty, not being affected by the acids, and producing an inflammable air when heated with a fixed alkali. It is probably a carburet of iron, either previously existing in the iron ore, and separated during the fusion, or formed by the combination of carbon with a portion of iron. A similar substance, as Bergman announced, is precipitated during the solution of some kinds of cast iron in diluted sulphuric acid.

Iron combined with a much smaller proportion of carbon forms Steel. Different methods are followed to form this combination: the product varies according to these, and also from the introduction of other substances.

The general method of forming steel, is by the process of cementation. A furnace is constructed of a conical form, in which are two large cases or troughs of fire-brick, capable of holding some tons of iron. Beneath these is a long grate, on which the fuel is placed: on the bottom of the case is laid a layer of charcoal dust; over this a layer of bars of malleable iron; over this again, a layer of charcoal powder, and alternate layers of charcoal and iron are thus raised to a considerable height: the whole is covered with clay to exclude the air, and flues are carried through the pile from the furnace, so as to communicate the heat more equally. The fire is kept up for eight or ten days. The progress of the cementation is discovered by withdrawing a bar from an aperture in the side: if the conversion of the iron into steel appear to be complete, the fire is extinguished, and the whole is left for six or eight days to cool.

Steel prepared in this manner, is named Blistered Steel, from the blisters which appear on its surface. To render it more perfect, it is subjected to the action of the hammer, in nearly the same manner as in the manufacture of forged iron: it is beat very thin, and is thus rendered more firm in its texture. Another mode of improving its quality, is to expose the bars of blistered steel to heat in a furnace sufficient to soften them, when they are welded together, doubled and drawn out, and sometimes welded again, forming what is named Shear Steel. Steel is rendered still more perfect, by fusing the bars of common blistered steel with a little charcoal powder, and a flux of pounded glass in a large crucible, placed in a wind furnace, the steel being rendered harder or softer as more or less of the flux is employed. When the fusion is complete, it is cast into small bars or ingots, and is named Ingot Steel. Even this steel is for some purposes farther subjected to the action of the hammer, by which its texture is rendered more compact; and this gives steel in its most valuable form*.

Steel is generally prepared from malleable iron. It can also be formed from some kinds of crude iron, particularly of the grey crude iron: the black crude iron furnishes a steel

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* Manchester Memoirs, vol. v.

that is too brittle. The crude iron from the sparry iron ore, is well adapted to this conversion. The steel thus obtained is named Natural Steel; but it is inferior to that obtained by cementation from forged iron.

From the mode in which steel is formed from iron, it must appear probable that the change is owing to the combination of carbon. The truth of this was established by Bergman by a series of excellent experiments. He found, that in dissolving malleable iron in diluted sulphuric acid, a larger quantity of hydrogen gas was evolved, than from the solution of the same weight of steel in the same acid; about 50 ounce measures of hydrogen being obtained from the solution of the one, when, from the other, the quantity amounted only to 48 ounce measures. This shewed that less water was decomposed by the one than by the other,—a difference owing to the steel containing carbon, which did not contribute to this decomposition. This carbon was discovered by its separation, during the solution of the steel, in the form of a black shining powder, which Bergman found to be analogous to plumbago. From 200 parts treated in this manner, he obtained one part of plumbago *.

The experiments of Bergman were confirmed by those of Monge, Vandermonde, and Berthollet: they shewed also, that in the conversion of iron into steel there is an augmentation of weight; and they observed, that the quantity of carbon combined, cannot be estimated correctly from the quantity of plumbago deposited during the solution of the steel, as part of it is dissolved by the hydrogen disengaged during the solution †.

The quantity appears to be different in different varieties of steel. In general, an increase of weight is gained by the iron, amounting to from $\frac{1}{180}$th to $\frac{1}{140}$th of its original

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* Opuscula Physica, vol. iii.

† Memoires de l'Acad. des Sciences, 1786, p. 132.

weight. The more carbon is introduced, the steel is more brittle: and so much may be introduced, that the valuable qualities of steel are lost. The quantity of carbon is greater, not only according to the proportion of charcoal used in the cementation, but also as the temperature has been more highly raised. The presence of carbon in steel is shewn by a very simple experiment, that of letting fall a drop of nitric acid on polished steel, which leaves a stain, by dissolving the iron of the surface, and leaving the carburet of iron, or plumbago.

The combination of iron with carbon, so as to form steel, is attained, not only by the preceding processes, but likewise by fusing bar iron with charcoal in a crucible; different varieties being formed, according to the proportions. From a process for forming steel given by Clouet, it has been inferred, that at a high temperature, iron is capable of decomposing carbonic acid, and attracting its carbon. The process consists in exposing to a strong heat in a crucible, iron in fragments, with one-third of its weight of carbonate of lime, and the same proportion of argil *. Mr Muschet, in repeating this process †, however, found the product to be different in its properties from steel, though at the same time the iron was altered in its qualities: it was harder, but possessed of less tenacity and elasticity. Sir George Mackenzie has remarked, that the substance obtained in this way from some kinds of iron, is analogous to steel, in becoming very hard when heated red-hot and plunged into cold water; and has supposed, that these properties may be acquired from some combination of the earths with iron,—a conjecture confirmed by the fact, that steel generally contains a portion of silex ‡.

Guyton supposing, that it is not charcoal that enters in-

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* Nicholson's Journal, 4to, vol. iii. p. 131.

† Philosophical Magazine, vol. xii. p. 27. 97.

‡ Nicholson's Journal, 4to, vol. iv. p. 109.

to the composition of steel, but pure carbon; and that from this the great hardness of steel is derived, performed the experiment of converting malleable iron into steel, by exposing it to an intense heat with a small diamond *. This experiment was executed with a result still more satisfactory by Sir George Mackenzie, the product being proved to have all the characteristic properties of steel †. It has since been repeated by Mr Children, diamond powder being inclosed in malleable iron wire, which was placed in the circuit of a galvanic battery: the presence of any other matter was thus excluded; the result was the formation of very perfect steel, from a heat even not intense.

Bergman had observed, in his analysis of steel, that some varieties of it contained portions of silica and manganese; and those ores of iron which contain manganese have been believed to be best adapted to the production of steel. The quantity of manganese, if it is present, which it may sometimes be as an adventitious ingredient, had certainly been greatly over-rated by Bergman. Vauquelin, repeating the analysis, with the improved methods which his skill in such researches suggested, did not discover manganese, but silica and phosphorus. Arsenic too, has been supposed to improve the quality of steel, and a particular variety of cast steel from India, Wootz, as it is called, has been said, on the authority of Mr Tennant, to contain this metal. It is a just observation by Gay Lussac, that these and other foreign substances may by intermixture add to the rigidity and hardness of steel, but they can scarcely be regarded as of essential importance.

The following table gives Vauquelin's results of the analysis of four different specimens of steel ‡.

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* Nicholson's Journal, vol. iii. p. 358.

† Ibid. vol. iv. p. 105. ‡ Ibid. vol. i. p. 252.

	No. 1.	No. 2.	No. 3.	No. 4.
Carbon,	0.00789	0.00683	0.00789	0.00631
Silica,	0.00315	0.00273	0.00315	0.00252
Phosphorus,	0.00345	0.00827	0.00791	0.01520
Iron,	0.98551	0.98217	0.98105	0.97597
	1.00000	1.00000	1.00000	1.00000

Steel is of a grey colour: when heated, its surface assumes different tints of colour, yellow, brown, purple, and blue, according to the temperature. These changes, it has been proved, arise from oxidation, as they do not occur if the steel is equally heated with the exclusion of oxygen, as under pure quicksilver, or in nitrogen gas; and the different colours either denote different degrees of oxidation, or are the effect of the thickness or mechanical structure of the thin films which are formed. The fracture is granular: it is brilliant, and is susceptible of a very high polish, which, from its hardness, it preserves: it is more fusible than iron: it is both ductile and malleable, and, when hammered at a high temperature, it can be extended into thinner plates than iron can. Cast steel is incapable of welding. When hammered, its specific gravity becomes greater, and its ductility and elasticity are increased. The specific gravity of bar steel is about 7.3 or 7.4; that of the same steel hammered 7.7.

The property which characterizes steel, and gives it its high value, is that of becoming extremely hard, by being plunged, when hot, into cold water; the hardness acquired is greater as the steel has been hotter and the water colder. The effect produced by this rapid reduction of heat is mechanical: the particles being suddenly approximated and united, that arrangement which would arise from their slow approximation, and produce softness and ductility, is prevented. Hence, steel hardened in this manner may have its softness and ductility restored, by heating it, and allowing it to cool slowly.

The harder steel is, it is also the more brittle; and hence, for the various uses to which it is applied, it must be made of different degrees of hardness; for although an excess of this quality alone might not be hurtful, yet the correspondent brittleness would, for certain purposes, render it useless. This gives rise to what is termed Tempering of Steel, which is nothing but the art of giving it any requisite degree of hardness. The method of effecting this formerly practised, was first to harden the steel, by plunging it when hot into cold water; and then to reduce it to the desired temper, by heating it slowly, and allowing it to cool gradually. The colours which appear on the surface of the metal when heated, indicate certain degrees of hardness, which will be possessed by it when cold: the straw colour, for instance, indicating the proper hardness for cutting instruments; and the blue, the temper for springs, or any instrument which requires to be elastic. An easier method of giving the requisite temper has been introduced. The pieces of steel are covered with oil or tallow, or put into a vessel containing either of these ingredients, and heated over a moderate fire. The appearance of the smoke from the oil or tallow indicates the degree of heat. If the smoke just appear, the temper corresponds with that indicated by the straw colour when the metal is heated alone. If so much heat is applied, that a black smoke arises, this points out a greater hardness; and thus proceeding till the vapour catch flame. By this method, a number of pieces may be done at once, with comparatively little trouble, and the heat is also more equally applied *.

Steel has a degree of hardness superior to that of any metal. It is also possessed of the highest elasticity, and

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* Philosophical Magazine, vol. ii. p. 97.

is capable of taking a very fine polish. The combination of these properties adapts it to many uses, and gives it its high value.

Iron is combined with Sulphur, when the temperature is raised so as to melt the latter. Thus, if a roll of sulphur be applied to a bar of iron red hot, they combine, and, as the compound is very fusible, the iron is melted. Or the combination is easily made, by exposing to a moderate heat, a mixture of iron-filings and sulphur. It is accompanied with a brilliant illumination, similar to that which, it has already been remarked, takes place in the combination of copper and sulphur. Native sulphuret of iron is an abundant mineral production.

The proportions of iron and sulphur in the sulphuret of iron, artificially formed, are different from those which exist in the natural sulphuret. In the latter they were stated by Proust at 47 of sulphur and 53 of iron; Mr Hatchet, in the analysis of different varieties of pyrites, obtained proportions differing a little, but on an average, they may be stated at 53 of sulphur and 47 of iron. In the artificial sulphuret, the sulphur is in much smaller proportion, not exceeding, according to Proust, 37.5 in 100 parts of the compound; nor is it easy to bring a larger proportion into combination by the direct fusion of iron and sulphur; but it can be done by again fusing the sulphuret, obtained by the usual process, with an additional proportion of sulphur. A compound is then formed analogous to the natural sulphuret. There also exists in nature, a compound analogous to that which contains the smaller proportion of sulphur. It forms what has been named Magnetic Pyrites, from its magnetic quality, and consists, according to Mr Hatchet's analysis of it, of 37 of sulphur and 63 of iron. In these two compounds, the proportions of sulphur may be inferred to be in the ratio of 1, 2, 100 of iron being combined in the one with 58.7 of sulphur; and in the other with 113. The deviation from the precise ratio is probably to be ascribed to the analysis not being perfectly accurate. And accordingly, Berzelius assigns from experiment, the proportions in the one at 63 of iron and 37 of sulphur, or 100 with 58.73, and in the other at 46.68 and 53.92, or 100 with 117 *. They may be distinguished by the names of sulphuret and super-sulphuret of iron.

Proust supposed that sulphur and iron combine only in these two proportions †. By varying the proportions, however, intermediate combinations may be formed, and even less sulphur, as 26 to 100 parts, may exist in the compound. Mr Hatchet has shewn, that when the proportion of sulphur does not exceed 37 in 100, the compound is magnetic; when it amounts to 45, it is capable of being attracted by the magnet; when equal to 53, the magnetic power is destroyed ‡.

The properties of sulphuret of iron are different according to the proportions. When the sulphur is in small proportion, the compound has a grey colour intermixed with purple and yellow, with a degree of metallic lustre; and when it has been formed by fusion, a crystalline texture. It is brittle, and gives a black powder. It is also very fusible. When the proportion of sulphur is larger, the product approaches more in appearance to the natural pyrites: its colour is yellow; and its lustre is greater. Exposed to heat in close vessels, a considerable part of the sulphur may be volatilized. The sulphuret, when moistened and exposed to air, is decomposed, oxygen being absorbed, and sulphate of iron formed. When diluted muriatic or sulphuric acid is poured upon it, there is a disengagement of sulphuretted hydrogen; the acid enabling the iron to decompose the water; and the hydrogen

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* Philosophical Magazine, vol. xli. p. 277.

† Nicholson's Journal, 8vo, vol. 1. p. 269.

‡ Philosophical Transactions, 1804, p. 356.

evolved, in consequence of this decomposition, dissolving a portion of the sulphur. The super-sulphuret does not exhibit the same phenomena, either on exposure to humidity, or to the action of diluted acids; the affinity of the sulphur to the iron being probably so far aided by its quantity as to maintain the combination, and resist the oxidation of the metal.

Iron and sulphur even act on each other, at a low temperature, when moistened. If a mixture of iron-filings and sulphur in this state be exposed to the atmosphere, oxygen is absorbed,—an absorption which would not happen from the action of the sulphur or iron alone. If the air be excluded, the water is decomposed.

The alkaline sulphurets appear to be capable of combining by fusion with iron; and their aqueous solutions, in which the sulphur exists in the state of a sulphuretted hydro-sulphuret, dissolve a portion of iron-filings, when boiled on them. From this solution, acids throw down a hydro-sulphuretted oxide of iron. Sulphuretted hydrogen, and the hydro-sulphurets, cause the deposition of a black precipitate from the solutions of iron.

Iron combines with Phosphorus, by exposing to heat in a crucible equal parts of iron filings and concrete phosphoric acid, with a third of their weight of charcoal powder; or by projecting pieces of phosphorus on iron at a red heat. The phosphuret of iron is of a white colour, has a granular fracture, is brittle and fusible: it consists, according to Berthier, of 20 of phosphorus and 80 of iron. Bergman having obtained this substance from that variety of iron named Cold Short Iron, by solution in diluted sulphuric acid, considered it, as has been already stated, as a peculiar metal, to which he gave the name of Siderite; and as the cause of the cold short property. Scheele and Klaproth discovered its real nature.

Iron combines with a number of the metals, but there are only a few of these alloys applied to any useful purpose. Its alloy with gold is very hard, and has considerable ductility and malleability: its colour is a dull grey, or, if the proportion of iron much exceed that of the gold, white. From the affinity between the two metals, gold can be used as a solder to unite pieces of steel. Iron and silver may be combined by fusion. According to an experiment on this combination by Guyton, they have a tendency to separate when kept in fusion, and arrange themselves according to their specific gravities: each of the metals, however, retains a portion of the other: the silver becomes sensibly magnetic, and the iron is altered in its properties; it becomes harder and more brittle, and when dissolved in nitric acid, gives a precipitate on the addition of muriatic acid. Though platina in its native state is alloyed with iron, it is scarcely practicable to combine them together, owing to their great infusibility. Lewis found that cast iron might be combined by fusion with platina: it produced an alloy extremely hard. With quicksilver iron can scarcely be combined, the iron not being changed, when the mercury is applied to its surface. The combination, however, can be effected by some indirect methods. Thus, by rubbing iron-filings with twice their weight of alum, and adding rather more of quicksilver than the weight of the alum, continuing the trituration with the addition of a little water for an hour or two, an amalgam is formed, in which the combination appears to be progressive for some time, as it continues to swell and split *. Mr Aikin likewise succeeded in forming an amalgam of iron, by uniting an amalgam of zinc and mercury with iron-filings, and adding to this muriate of iron: the zinc attracts the oxygen and muriatic acid from the iron, and the quicksilver and iron unite †. The alloy of iron with

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* Crell's Chemical Journal, vol. ii. p. 105.

† Philosophical Magazine, vol. xiii. p. 406.

copper is not very perfect: it is of a grey colour, brittle, and not very fusible. It is applied to no use.

The qualities of which iron in its various forms is possessed, render it applicable to numerous purposes of utility. In hardness no metal is equal to steel, and no substance, in combination with this quality, possesses such a degree of tenacity; hence its adaptation to the fabrication of cutting instruments. It is equally superior in elasticity,—a quality from which it is the spring of motion in more delicate machinery. The toughness of malleable iron adapts it to purposes where strength is required; while the singular combination of its infusibility, with its property of softening by heat so as to admit of a close assimilation and union of its parts, renders it at once capable of being worked, and of bearing the most intense heat. Surveying the applications of this metal, in the fabrication of tools and instruments, in the construction of time-pieces, in the magnetic needle, and in the numerous other uses to which it is applied, it must soon be perceived, that it is superior to all the metals in real value,—a value well displayed in the superiority it confers on civilized nations, and in the slow progress of the arts of life in barbarous tribes unacquainted with its use.

CHAP. XI.

LEAD.

This metal has considerable lustre, which is quickly lost, however, on exposure to the air. It is the softest and least elastic of all the solid metals: it has so little ductility, that it cannot be drawn into fine wire; and a wire of it one-tenth of an inch in diameter, cannot support more than 30 libs. without breaking. It is more malleable, and may be beat into thin leaves. Its specific gravity is 11.352. Its taste and smell, when it is rubbed, are peculiar and rather disagreeable; and it is one of those metals which prove highly noxious to animal life. It occurs in nature, mineralized by sulphur, by carbonic, sulphuric, phosphoric, arsénic, and molybdic acids.

The sulphuret, galena as it is named, is the ore from which nearly all the lead of commerce is procured. The extraction of the metal is very easy. The ore pounded, and freed from the admixture of any stony matter by washing, is fused in a furnace with the addition of lime, which combines with the sulphur of the sulphuret; the lead is melted and run out at an aperture towards the bottom of the furnace. When the native salts of lead are found with the galena, so as to render it of importance to work them, they are roasted to expel the volatile matter, and are afterwards fused in contact with the fuel, with an addition of lime. The lead obtained from galena, sometimes contains so much silver, as to be subjected to an additional process to separate the silver. The lead is oxidated on the hearth of the refining furnace; a current of air being directed on its surface when in fusion, by bellows, by which the oxidation is accelerated, and the oxide is semi-vitrified, forming what is named Litharge; by the blast of air, this is driven towards an aperture in the furnace, where it is allowed to flow out: the silver remains with a small portion of lead, from which it is afterwards freed by cupellation; and the oxide of lead is either sold in commerce, or is reduced to the metallic state *.

Lead melts at a temperature inferior to ignition, equal, according to Newton's calculation, to about 540 of Fahrenheit. Dr Irvine, by the mercurial thermometer, found

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* An account of this process is given in Aikin's Chemical Dictionary, article Silver, and in Nicholson's Journal, vol. xv. p. 1.

its fusing point to be 594 *. By the usual process for obtaining metallic crystallizations, it can be obtained in the form of a tetraedral pyramid, single or double. At a very high heat it is volatilized.

Lead is very susceptible of oxidation. When first fused its surface is bright; but in a short time, if the air is not excluded, it becomes dull, is covered with a thin film, which increases in thickness, forming a grey powder. If this be withdrawn, the same phenomena are again presented, and thus the whole of the lead may be converted into this powder. By exposing it to a higher heat, with the access of air, it becomes yellow of various shades, and at length acquires a lively yellow colour, forming the pigment named *Massicot*, in which the metal is more highly oxidated. By continuing the heat, raising it a little, and causing the flame to play upon the surface, while the powder is constantly stirred, the yellow colour changes to a red, which, when the process is carried on in the large way, and with particular management, becomes very bright: this forms the pigment named Red Lead, or *Minium*. By applying the heat quickly with a current of air blown over the surface of the metal, the oxide is semi-vitrified, forming the soft flaky substance *Litharge;* a product generally obtained in the process of extracting silver from lead. By a stronger heat, this may be completely vitrified, when it forms the Glass of Lead.

In these changes two specific degrees of oxidation are supposed to be established. The grey powder formed on the surface of melted lead is, according to Proust, the yellow oxide with an intermixture of metallic lead, and is not therefore a definite compound. The yellow oxide is so, when it is obtained uniform, and it is best obtained in this state by precipitation from some of the salts of lead, of the greater number of which it is the base,—by precipitation,

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* Chemical Essays, p. 35.

for example, from nitrate of lead by potash, or by carbonate of ammonia, and exposure of the precipitate, well washed, to a heat sufficient to expel the water or the carbonic acid. The red is at a higher degree of oxidation, as is evident from the yellow being converted into it by continuing the calcination, and from its being reduced by a higher heat to the yellow oxide, with a disengagement of oxygen. Litharge, Dr Thomson found to consist of the yellow oxide, with about 4 parts of carbonic acid in 100; and both it and the Glassy Oxide seem to owe their peculiar appearance to the state of aggregation.

Besides these there is another oxide of lead, in which the metal is in a higher degree of oxidation, the Brown Oxide as it is named. It was discovered by Scheele, and is obtained, according to his method, by digesting the red oxide with diluted nitric acid; it is changed in the state of oxidation by the action of the acid, part passes into the yellow oxide which is dissolved by the acid, and the remainder assumes a brown colour, and forms the brown oxide. It may also be formed by a process given by Vauquelin, transmitting oxymuriatic gas over the red oxide suspended in water until it is dissolved, and then precipitating the solution by potash.

The proportions of oxygen in these oxides have been variously determined. Vauquelin supposed that the protoxide contains 7 *per cent.* of oxygen. Proust inferred, that the yellow oxide, obtained by decomposing nitrate of lead by potash, contains 9 *per cent.* of oxygen. Dr Thomson stated the proportion at 10.3, and that in the red at 12. And the brown, according to Proust, contains 21 of oxygen in 100 parts. The estimate of 7 in the yellow oxide appears to be just. In the formation of the red by calcination, the metal increases in weight between 10 and 11 parts in 100. And the brown oxide is stated to lose between 6 and 7 of oxygen, when it is reduced by heat to the yellow. These results would give the proportions of

7, 10½, and 14, or the series of 1, 1½, 2 *. This has accordingly been established on the authority of Berzelius, with some slight variations in the proportions. By experiment he finds the yellow oxide to be composed of 92.85 of lead, and 7.15 of oxygen, or 100 with 7.7; the red of 90 and 10, or 100 with 11; and the brown of 86.51 and 13.49, or 100 with 15.6, proportions very nearly in the series now stated †.

This series would lead to the conclusion, that a lower degree of oxidation of the metal exists,—that doubling the above numbers, or considering them as 2, 3, and 4, there will be a lower oxide, containing a proportion of oxygen as 1. But no such oxide has been established. From the equivalent number derived from the salts of lead, it has farther been inferred, that the yellow oxide must be the protoxide. To get rid, therefore, of the absurdity which this implies in the atomic hypothesis, of the red oxide, as it is intermediate between the yellow and the brown, being composed of 1 atom of lead, with 1½ atom of oxygen, it has been supposed that it is not a compound of the metal with oxygen, but a compound of these two oxides, a supposition certainly rather improbable.

The oxides of lead have considerable specific gravity: they are tasteless and insoluble in water: they act as powerful fluxes on earthy matter. The yellow oxide melts readily, and forms a yellowish semi-transparent glass; exposed to the air at a moderate heat, it absorbs oxygen, and passes into the red. It dissolves readily in acids, and forms the base of the greater number of the salts of lead. It is also dissolved by alkalis. The red oxide is partially decomposed by heat, giving out oxygen, and passing into the yellow oxide, and, if the heat be strong, suffering vitrification. It does not dissolve in acids, but is decomposed,

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* Elements of Chemical Philosophy, p. 596.

† Philosophical Magazine, vol. xli. p. 7. 545.

either giving out oxygen gas, and passing into the yellow oxide, which combines with the acid, or being resolved into the yellow and brown oxides, the latter of which is precipitated. The brown oxide is of a deep brown colour; when decomposed by heat, it affords oxygen, and melts into a glass: it also gives out oxygen, when acted on by sulphuric acid: it is not soluble in nitric, but dissolves in nitrous acid: with muriatic acid, it forms oxymuriatic gas: it also decomposes ammonia,—properties which shew its excess of oxygen *. All the oxides of lead are easily reduced to the metallic state, by exposure to heat with carbonaceous matter, or by heating them in hydrogen gas.

Lead does not decompose water, so as to produce any sensible disengagement of hydrogen gas. But when kept immersed in water, it is covered with a white efflorescence or crust, produced probably by the action of the oxygen, which water holds loosely dissolved. Guyton has stated some rather singular, and, if they are accurate, important results with regard to this. Water purified from saline matter by distillation, acts rapidly on lead, so that the metal immersed in it is soon covered with a white crust, which precipitates. This is owing to the action of the atmospheric air which the water has imbibed, for it does not happen when the water has been deprived of air by boiling or by the air-pump; and it stops when the air contained in the water is exhausted, but is renewed when the air is admitted. The presence of any neutral salts, however, such as the sulphates or muriates, in very minute quantity, prevents this action, the presence, for example, of 0.002 of sulphate of lime is sufficient; and to this is owing the preservation of spring or river water in lead without change. The substance formed in this operation, Guyton regards as a compound of oxide of lead and water †.

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* Fourcroy's System, vol. vi. p. 122.

† Nicholson's Journal, vol. xxvi. p. 105.

The greater number of the acids act on lead, or combine with its oxides. Its saline compounds, which are soluble, are generally distinguished by a sweet styptic taste. These combinations can scarcely be formed with the metal at the *maximum* of oxidation; the red oxide, too, generally gives out part of its oxygen, when acted on by acids: and hence the yellow is their base. A plate of zinc precipitates from them metallic lead: sulphuretted hydrogen gives a very dark coloured precipitate; and sulphuric acid gives a white precipitate, which is reduced to the metallic state when heated by the blowpipe on charcoal.

Sulphuric acid scarcely acts on lead in the cold; but boiled on it, sulphurous acid is disengaged, and the metal being oxidated, combines with part of the sulphuric acid, and forms a white mass, in which there is an excess of acid. This is sparingly soluble in water: a small portion, however, is dissolved from the excess of acid: and by evaporation, needle-like crystals are obtained. The neutral sulphate is obtained by decomposing any of the soluble salts of lead, by sulphuric acid, or rather by an alkaline sulphate. It is precipitated in a dense white powder, which is almost insoluble, or, at least, requires above 1000 parts of water for its solution. According to Kirwan's estimate, it consists of 75 of oxide, (composed of 71 of lead and 4 of oxygen), 23.37 of acid, and 1.63 of water. According to Berthier, sulphate of lead, freed from any adhering water by a moderate calcination, contains 26 of acid and 69 of metal, leaving five as the proportion of oxygen united with the lead; a result with which its analysis by Klaproth and Berzelius corresponds. This compound exists native in a crystalline form.

Sulphurous acid does not act on lead; but Fourcroy and Vauquelin found, that by placing the red oxide in contact with this acid, it became white, and a saline mass was formed, containing both sulphate and sulphite of lead. The latter, they also found, can be obtained pure, by adding the white oxide obtained from the nitrate, to slphurous acid. It is in the form of a white powder, insoluble in water. Both it and the sulphate are partially decomposed by heat, and, when heated on charcoal by the blowpipe, are reduced.

Nitric acid, a little diluted, acts on lead; nitric oxide gas is disengaged, and the metal is oxidated. This oxide combines with the acid, and forms a soluble salt: the solution by evaporation deposites crystals, which appear to be octohedral: they are white, with a degree of adamantine lustre, and are semi-transparent. They deflagrate when thrown on burning fuel, and are decomposed when exposed to heat alone, the acid being partly expelled, partly decomposed, and the oxide being vitrified. A yellowish white precipitate is thrown down from it by the alkalis. It consists, according to Dr Thomson's analysis, of 66 of oxide, and 34 of acid and water *: according to Chevreul's, of 67 of oxide and 33 of acid. The oxide in this salt appears to be the yellow oxide; and this oxide, added to the acid, is at once dissolved in it. When nitric acid is poured on the red oxide, the oxide is not dissolved, but the degree of its oxidation is changed: it becomes, as Proust has observed †, at first white, and a portion of it suffers solution, but another part, about one-seventh of it, acquires a brown colour, and remains insoluble; forming the peroxide, while the salt in solution is similar to that formed by the direct solution of lead in nitric acid. A solution in which, according to Proust, the metal is in a lower state of oxidation than the yellow oxide, may be obtained, by boiling a solution of the nitrate on a quantity of metallic lead. From being colourless it becomes yellow, and when cold deposites crystals in thin plates, which are less soluble

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* Nicholson's Journal, 8vo. vol. viii. p. 285.

† Journal de Physique, tom. lvi.

in water than the other nitrate. According to Dr Thomson's experiments, this salt rather differs in the proportion of the acid; the proportions he assigns are 81.5 of oxide, with 18.5 of acid and water. By exposing either to heat, so as to cause a partial expulsion of the acid, a sub-nitrate is obtained in the form of a yellow powder, consisting of 86 of oxide, and 14 of acid and water *.

These nitrates of lead have been more minutely investigated by Chevreul and Berzelius, and present some rather complicated results. From Chevreul's experiments, there appear to be two nitrates of lead; the one formed by the solution of the metal in the acid, which crystallizes in octohedrons, and which is a super-nitrate composed of 33 of acid and 67 of yellow oxide, or 100 with 203, the other the neutral nitrate, formed by boiling the solution of the super-nitrate with a portion of yellow oxide, and composed of 19.86 of acid, and 80.14 of oxide, or 100 with 403. This last is in scales of a pearly lustre, and may be obtained in small needles; its taste is sweet and astringent. When a solution of super-nitrate is boiled on metallic lead, a portion of the metal is oxidated at the expence of the nitric acid, which thus passes into nitrous acid, and combines with the oxide; the solution acquires a yellow colour, which disappears on continuing the boiling, and a salt is obtained in needles, which are of a reddish yellow colour, and easily soluble in water. This is a sub-nitrite. If the boiling be stopt while the yellow colour of the solution remains, a salt is obtained, on cooling, in crystalline scales of a yellow colour, less soluble than the other, and similar to the salt observed by Proust. This is the nitrite of lead; it is obtained still better by decomposing partially the subnitrite, by passing a current of carbonic acid gas through its solution. It is composed of 18.15 of acid, and 81.85 of oxide, or 100 with 450. The sub-nitrite consists of 9.9

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* Nicholson's Journal, 8vo, vol. viii. p. 285-8.

of acid, and 90.1 of oxide, or 100 with 910. All these four salts, therefore, conform to the law of saline combinations, that the higher proportion of one of the ingredients is twice that of the lower. Between these salts, however, Chevreul adds there are intermediate ones, whether compounds of them or not it is difficult to determine. Similar results were established by Berzelius *.

Muriatic acid acts very feebly on lead, even when assisted by heat. With the oxide it combines more easily, when the oxidation is not at the maximum; when digested on the red oxide, it decomposes it, abstracts part of its oxygen, and forms oxymuriatic acid, while another part of it combines with the metal thus partially de-oxidated. In these combinations there is always an excess of acid, which communicates solubility, and enables the salt to crystallize in small prisms, having a silky lustre. The neutral muriate is best obtained by adding muriatic acid, or rather a muriate, to the solution of any of the soluble salts of lead, adding, for example, muriate of soda to nitrate of lead. The muriate of lead is precipitated. It is soluble in about 30 parts of water, and by concentration of its solution, slender prismatic crystals are obtained. It is fused by heat, and forms when cold, after its fusion, a grey semi transparent mass, named Horn Lead. If the heat be continued, it is partly decomposed, partly sublimed. According to Kirwan, the crystallized muriate consists of 81.77 of oxide, and 18.23 of acid and water. The fused muriate, or Horn Lead as it is called, consists, according to Berzelius, of 19.18 of acid, and 80.82 of yellow oxide of lead. Considering it as a chloride, it is composed, according to Dr J. Davy, of 25.78 of chlorine, and 74.22 of lead. The same substance is formed when lead is heated in oxymuriatic acid gas.

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* Annales de Chimie, tom. lxxxiii. p. 1. 57. tom. lxxxiv. p. 1. Philosophical Magazine, vol. xliii.

Oxymuriatic gas transmitted through water over red oxide of lead, brings a portion of it to a higher state of oxidation, which remains insoluble, while, with another portion of the oxide, it enters into combination, forming what has been regarded as an oxymuriate, and which is more soluble than muriate of lead: the solution has a yellowish colour, and affords by the action of soda or potash a brownish red precipitate.

Phosphoric acid acts on lead slowly. But the phosphate of lead is formed by adding a solution of phosphate of soda to a solution of nitrate or acetate of lead; it is thrown down in a white, flaky precipitate. It is insoluble in water; it dissolves in nitric acid; muriatic and sulphuric acids decompose it. It consists, according to Berthier, of 77.5 of oxide, and 22.5 of acid *; according to Berzelius, of 76 of oxide and 24 of acid. Besides the neutral phosphate, Berzelius has given the composition of a super-phosphate and a sub-phosphate. The former is obtained by adding to a hot and concentrated solution of muriate of lead, a solution of super-phosphate of soda; it consists of 69.73 of oxide, and 30.27 of acid. The latter is formed by digesting phosphate of lead with caustic ammonia: it consists of 82.52 of oxide, and 17.48 of acid †. The neutral phosphate exists native, usually crystallized in prisms of a green or yellow colour.

Phosphite of lead was formed by Berzelius, by adding to a solution of phosphite of ammonia, a hot concentrated solution of muriate of lead; it is thrown down in a bulky white precipitate: it consists of 80.22 of oxide, and 19.78 of acid.

Borate of lead is formed by adding borax to a solution of nitrate of lead; it forms a white precipitate, insoluble, which melts before the blow pipe into a kind of glass.

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* Journal des Mines, No. 152.

† Annales de Chimie et Physique, tom. ii. p. 160.

Carbonic acid exerts an affinity to the oxides of lead, and the carbonate of lead can be formed by adding a solution of carbonate of soda or potash to a solution of any of the soluble salts of lead, a copious white precipitate being formed. The paint named Cerusse or White Lead is a carbonate or sub-carbonate. It is prepared by exposing lead in thin sheets, coiled and inclosed in an earthen vessel, to the vapour of vinegar, the heat being usually applied so as to produce this vapour, by placing the vessels in stable-litter, or tanner's bark: the metal is oxidated, and the carbonic acid is either formed from the deomposition of part of the acetic acid, or is absorbed from the air. Carbonate of lead likewise exists native, usually crystallized in prisms or tables. The results of a number of analyses of it, agree in fixing its proportions at 16.5 of acid, and 83.5 of oxide of lead.

When cerusse is boiled with vinegar, a salt is formed, the sugar of lead of commerce, which is obtained by evaporation crystallized in prisms. This, as a compound of acetic acid, is to be afterwards considered.

Iodine acts on lead when heat is applied; and when hydriodate of soda is added to a solution of a salt of lead, an analogous product is obtained; it is of a fine orange yellow colour, and insoluble in water.

The salts of lead are decomposed by the alkalis, which throw down from their solutions precipitates, which are sub-salts, as Vauquelin has observed *. Potash or soda added in excess, re-dissolve part of the precipitate: they are also capable of dissolving the pure oxides, and they seem even to favour the oxidation of the metal by water or air. Some of the earths also, particularly lime, when boiled with water on the oxides of lead, dissolve a portion; the solution affording minute crystals on evaporation. All the earths unite with these oxides by fusion, and form

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* Nicholson's Journal, 4to, vol. iii. p. 475.

yellow glasses or enamels: and no metallic oxide is so powerful in promoting the vitrification of earthy substances as oxide of lead.

Oxide of lead, from the strength of its attraction to acids, is capable, when aided by circumstances, of decomposing a number of the neutral salts. Thus, when triturated with muriate of ammonia, the pungent smell of the ammonia becomes apparent: if heat is applied, the ammoniacal gas is disengaged. It likewise decomposes muriate of soda: and this decomposition is of importance, as it has been employed as a method of procuring the alkali. It was first discovered by Scheele; he found, that, when four parts of litharge are mixed with one part of muriate of soda, and made into a soft paste with water, after some time soda is evolved, the acid being attracted by the oxide of lead; and by keeping the mixture soft, by the addition of water as it is necessary, the whole of the salt may be decomposed, and the soda extracted by lixiviation. The process has been carried on on a large scale; the compound of oxide of lead and muriatic acid being convertible by heat into a yellow paint, which in part defrays the expence. The theory of the operation is attended with some difficulty, for soda is capable of decomposing neutral muriate of lead, abstracting the acid from the oxide; and, of course, the oxide cannot be supposed to have a stronger attraction to that acid than the alkali, in consequence of which it decomposes the muriate of soda. Some chemists supposed the effect to be produced by the concurrent affinity of carbonic acid contained in the litharge, or derived from the atmosphere. Vauquelin referred it to the effect of the quantity of oxide of lead employed. Muriate of lead, he supposed, had an attraction to an excess of oxide; hence, in the decomposition which the oxide of lead effects in muriate of soda, two affinities operate, the affinity of oxide of lead to muriatic acid, and muriate of lead to an excess of oxide; and from this he explained why so much oxide was necessary to decompose the muriate of soda *. Without adopting this complicated view, the result may be ascribed to the attraction being exerted more powerfully by the oxide of lead to the acid in that proportion which forms the sub-muriate, aided also by the insolubility of the sub-muriate. In conformity to this explanation, it is found, that soda cannot deprive neutral muriate of lead of the whole of its acid, but abstracts only so much as to reduce it to a sub-muriate.

Lead forms no combination with Carbon. It unites with Sulphur by fusion, and forms a compound analogous to the native sulphuret, of a dark grey colour, having metallic lustre, brittle, with a striated texture, and less fusible than the metal. The proportions in which they combine appear to be, from the analysis by Berzelius, 86.51 of lead, and 13.49 of sulphur, or 100 with 15.6. But the proportions are various in native galena; and there seems to be one variety in which the proportion of sulphur amounts to about 25 per cent. and which may therefore be regarded as the second definite compound, or super-sulphuret of lead. By exposing sulphuret of lead to heat, much of the sulphur is volatilized. The circumstances of this decomposition have been examined by Descostils, principally with a view to the proper metallurgic treatment of this ore, as well as the sulphuretted ores of the other metals. When heat is applied in close vessels, with the exclusion of the air, a little sulphur only is separated; the greater part sublimes when the heat is strong, in the state of a sulphuret, with an increased proportion of sulphur, and a sub-sulphuret remains unsublimed. If the air is admitted, dense vapours arise, which have a strong odour of sulphurous acid, and deposite sulphate of lead; and metallic lead is the residuum †.

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* Nicholson's Journal, 4to, vol. iii. p. 470.

† Memoires d'Arcueil, tom. ii. p. 424.

It is uncertain whether sulphur can be combined with oxide of lead: when they are mixed and subjected to heat, the compound formed, as Vauquelin has remarked *, is similar to the metallic sulphuret; whence it appears, that the oxide is decomposed, its oxygen being attracted by a portion of the sulphur, and forming sulphuric or sulphurous acid, which the heat dissipates, while the remaining sulphur combines with the metal. The result of the action of sulphuretted hydrogen on the oxides of lead is nearly the same: when added to the solution of any of the salts of lead, a precipitate is formed, of a dark brown colour, approaching to black: this arises from the hydrogen of the sulphuretted hydrogen combining with the oxygen of the oxide, while the sulphur unites with the lead. The precipitate is also similar, as Vauquelin remarks, to the native sulphuret, containing only a little more sulphur, which may be separated by the application of heat. The action of the hydro-sulphurets, and probably of the sulphuretted hydro-sulphurets, is similar.

The solutions of the salts of lead are so deeply blackened by sulphuretted hydrogen, that they have been employed as a sympathetic ink: letters traced with a very dilute solution on paper, becoming visible when the paper is exposed to sulphuretted hydrogen gas. The action of sulphuretted hydrogen likewise affords a test by which the presence of lead may be detected; and as this test is sometimes used to discover the presence of lead in suspected wines or other liquors, it is of importance that it should be free from ambiguity. The solutions of the alkaline sulphurets, which have been used, are liable to some fallacy; for although they precipitate lead of a very dark colour, they also throw down iron when it is in certain states of oxidation. A test was given by Hahneman, as having the advantage of precipitating lead, but not iron. It is pre-

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* Nicholson's Journal, 4to, vol. v. p. 116.

pared from sulphuret of lime, (formed by exposing equal parts of sulphur and of oyster-shells to a white heat for 15 minutes), and super-tartrate of potash. 120 grains of the sulphuret, and 180 of the super-tartrate, are put into a bottle, which is to be filled with 16 ounces of water that has been previously boiled, and suffered to cool. The liquor having been repeatedly shaken, is to be poured off clear into phials, which hold about one ounce measure; into each of which about 20 drops of muriatic acid have been put; and they are well corked. One part of this solution, mixed with three parts of the suspected liquor, will discover, by a black precipitate, the smallest quantity of lead, while it does not precipitate iron; the tartaric and muriatic acids retaining iron in solution when combined with sulphuretted hydrogen *. Perhaps, however, the simple solution of sulphuretted hydrogen in water is less liable to fallacy than any other test. A solution of sulphate of soda affords also a good test, a white precipitate being formed when it is added to any liquor containing lead. And the utmost certainty is attained, by obtaining from any of these precipitates dried, and exposed to heat with a little charcoal in a small crucible, a globule of lead.

Lead combines with phosphorus, the compound being formed when phosphorus is projected on melted lead. The phosphuret has a colour approaching to that of lead, but whiter: it has metallic lustre, but is liable to tarnish: is soft, so as to be easily cut by a knife, flexible, and of a lamellated texture. Pelletier supposed it to contain, in 100 parts, from 12 to 15 of phosphorus. It is partially decomposed, and the phosphorus volatilized, during fusion before the flame of the blowpipe.

Lead combines with a number of the metals, but few of its alloys are applied to any useful purpose, that with tin excepted, which forms Pewter, and, in a different pro-

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* Crell's Chemical Journal, vol. iii. p. 61.

portion, what is named Soft Solder. It is easily united with gold by fusion, and, in Mr Hatchet's experiments, was found, even in a very small proportion, to impair greatly the ductility of the gold: it, at the same time, debases its colour. It unites with silver with equal facility, and promotes the fusion of the silver, the compound being very fusible: the tenacity and hardness of the silver are also much impaired. This is one of those alloys in which the density exceeds the mean density of the two metals. By a continued heat, sufficient to keep it in fusion, with exposure to the atmosphere, the lead is oxidated, leaving the silver pure. With platina lead combines, forming an alloy, in which the ductility of the platina is much diminished. By quicksilver it is dissolved, and a series of combinations formed, varying according to the proportions, the fluidity of the quicksilver being diminished, and the consistence becoming firm when the lead predominates, so as to admit of the compound assuming a crystalline arrangement. With copper, it forms a brittle alloy of a grey colour. It can scarcely be combined with iron; the two metals appearing to remain distinct even when both are brought into fusion. According to Guyton *, however, each receives a portion of the other; so that two alloys, one of iron with a little lead, and another of lead with a little iron, are formed.

The uses of lead are extensive. As it is flexible, easily reduced to thin sheets, and easily united by solder, it is used in making pipes for conveying water, large boilers, and vessels of different kinds. It is cast into thin sheets for covering buildings. Its oxides are used as paints. They are also employed in the manufacture of the finer kinds of glass, to which they communicate density, a higher refractive power, a greater equality of texture, and a greater susceptibility of polish: hence, they enter into

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* Annales de Chimie, tom. xliii.

the composition of the pastes which imitate the gems. They form, in combination with earthy matter, the glazing of the inferior kinds of earthen ware. There is some reason to doubt, whether the use of lead in pipes for conveying water, or in vessels for containing it, be altogether safe; lead, immersed in water, is covered at length with a white crust of oxide or carbonate; and this metal is the most insidious, and, at the same time, one of the most destructive of the mineral poisons. In water, however, which has been conveyed through pipes of lead, no trace of the metal can be discovered by the most delicate test, sulphuretted hydrogen. Even water kept in cisterns of lead, where the exposure to the air is more free, seems not to have in general any sensible impregnation; this may arise from the deposite of earthy matter from the water covering the lead. The observations of Guyton too, already stated, on the effect of the presence of a little saline matter in preventing its action on lead, may serve to explain how the practice of keeping water which is used as drink in cisterns of lead, is not more injurious than it appears to be. Some facts appear to prove, that river water is more liable to receive an impregnation from leaden vessels than spring water is, probably from the salts in the former being chiefly muriates, while in the latter they are sulphates or carbonates. The use of earthen ware glazed with oxide of lead is hazardous, as the glazing is soon eroded by any acid liquor, and a noxious impregnation communicated; and many fatal accidents have occurred from the use of lead in the fabrication of vessels in which wine, cyder, and other fermented liquors, are prepared or kept.

CHAP. XII.

TIN.

Tin, though a metal known from the most remote ages, is not widely diffused; it is found in few countries; principally in Cornwall in England; in Gallicia in Spain; in Saxony and Bohemia; in the peninsula of Malaca, and in Mexico. Its ores are comparatively few, there being only two species, the oxide and the sulphuret. The former of these is the only one wrought to obtain the metal. Being freed, by washing, from the intermixture of any stony matter, it is roasted, and then fused in contact with the fuel by a moderate heat. The tin of Cornwall is supposed to be purer than the German tin, but less pure than the tin from India.

This metal is of a white colour, with considerable lustre: it has so much malleability, that it can be reduced by beating into thin leaves: it has, however, little ductility, a wire, one tenth of an inch in diameter, not supporting more than 50 libs. without breaking. Its hardness is so inconsiderable, that it can be easily cut by a knife, and scratched by a number of other metals. It is flexible, and, in bending, gives a crackling noise: when rubbed, it emits a peculiar odour. It is one of the lightest of the metals; its specific gravity, after fusion, being 7.291; after hammering, 7.299. It loses its lustre from exposure to the atmosphere, but it does not rust from the action of air or water.

Tin melts at 416° of Fahrenheit; according to Crichton, at 442 *. When slowly cooled, it crystallizes in rhombs.

When in fusion, and at the same time exposed to the action of the air, it is quickly oxidated: its surface becomes dull, and is then covered with a grey powder: this is the metal in the first degree of oxidation; and has been said to contain 10 of oxygen in 100 parts. If it be longer exposed to heat, and stirred frequently, it becomes of a yellowish-white colour, from a higher degree of oxidation, and forms the substance named *Putty*, which is employed in polishing glass. When tin is exposed to a very strong heat in a crucible, or is subjected with an admixture of nitre to a temperature above ignition, it burns with a yellowish-white flame, and affords a similar oxide. This oxide is capable of volatilization, and it forms, in condensing, needle-like crystals. Precipitates are thrown down from the saline combinations of tin, in which the metal appears to be more highly oxidated. Proust supposed that the precipitate from the solution of tin in dilute nitric acid by potash, is an oxide containing about 22 parts of oxygen in 100 parts; and the white powder, formed by the action of concentrated nitric acid on tin, an oxide containing 28 of oxygen. Other results have since been established. Berzelius found, that the protoxide of tin cannot easily be obtained by direct oxidation of the metal by heat. He procured it by dissolving tin in muriatic acid, and precipitating the solution by potash or carbonate of potash; a white hydrate is formed, which, when the water is abstracted, leaves a black oxide. In this degree of oxidation, Berzelius inferred, by indirect methods, that 88.03 of the metal are combined with 11.97 of oxygen, or 100 with 13.6 †. The per-oxide is formed by submitting tin to the action of

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* Philosophical Magazine, vol. xv. p. 147.

† Nicholson's Journal, vol. xxxv. p. 124.

nitric acid; a white powder is formed as the action proceeds, which, when washed and dried, is of a light yellow colour. It consists, according to Berzelius, of 78.62 of tin, and 21.38 of oxygen, or 100 with 27.2 *. Gay Lussac had assigned to these two oxides, proportions precisely the same †. Berzelius had farther supposed, that the oxide which is obtained from the concentrated muriate of tin, long known by the name of *Spirit of Libavius*, is at an intermediate degree of oxidation. Gay Lussac shewed, that it is the same with the oxide formed by nitric acid ‡; and Berzelius admits this, while, at the same time, he points out differences in the chemical properties of these oxides, arising probably from their state of aggregation; the oxide, from the action of the nitric acid, being much less easily dissolved in acids than the other ||.

The black oxide of tin has a great tendency to pass to a higher state of oxidation. When heated at the flame of a candle it takes fire, and continues to burn. The yellow oxide is very permanent. When it has been washed with the greatest care, it gives a red colour to litmus; and this cannot be ascribed to acid adhering to it, as the water poured from it has no reddening effect. Berzelius has therefore supposed that it might be ranked as an acid, especially as it also combines with the alkalis. But its property of combining with and neutralizing acids precludes this conclusion. After being heated, it loses this reddening power: and the property, therefore, can be ascribed only to the hydrate.

The oxides of tin retain water, or the elements of water, in considerable proportion, forming hydrates. The black oxide, when it is precipitated from its salts, is of a white

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* Philosophical Magazine, vol. xliii. p. 93.

† Annales de Chimie, tom. lxxx. p. 169.

‡ Annales de Chimie et Physique, tom. i. p. 43.

|| Ibid. tom. v. p. 153.

colour, and when heated gives out water. When the peroxide formed by the action of nitric acid is washed and dried at a heat of 130, it forms, Dr Thomson has remarked, a white semi-transparent friable hydrate, composed of 80.64 of oxide and 19.36 of water, or 100 with 24: when it is dried in the open air without heat, it forms a hydrate remarkable for the beauty of its white colour, and its silky lustre, which contains twice the quantity of water, or 100 with 48 *.

Tin is oxidated and dissolved by the greater number of the acids; and in these combinations, is particularly displayed the tendency of this metal to pass to a highly oxidated state. Its saline solutions are from this property capable of abstracting oxygen from many substances; and from the same cause they are not permanent; the metal, continuing to attract oxygen from the acid, or from the air, becomes so highly oxidated, that its affinity to the acid is weakened, and it separates in the state of a compound with excess of base.

With the assistance of a moderate heat, tin decomposes sulphuric acid, attracts oxygen from it, and disengages sulphurous acid gas; if the heat be high, even a portion of sulphur is evolved. The solution deposites slender crystals: it is decomposed by the affusion of water, which throws down a white precipitate. If much of the tin has been dissolved, the solution is gelatinous. It is decomposed by heat; and when kept for some time, the oxide attracts so much oxygen as to become insoluble. When the solution is made with a diluted acid, and in the cold, it is more permanent, and is not decomposed by water, partly from the lower state of oxidation, and partly probably from having an excess of acid.

Fourcroy and Vauquelin examined the action of sulphurous acid on tin: when immersed in the liquid acid, it

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* Annals of Philosophy, vol. x. p. 149.

assumes a yellowish colour, afterwards becomes black, and a black powder is produced, which appears to be a sulphuret of tin, formed from the decomposition of the acid. Part of the tin being thus oxidated, combines with the acid, and this white sulphite, with a portion of sulphur in combination with it, is precipitated in the form of a white powder. A part of the oxide of tin also remains in solution in the liquid, combined with the remaining sulphurous acid *.

If nitric acid concentrated, or of a specific gravity about 1.48, be poured on tin filings, there is no apparent action; but if it be a little diluted, or if a very little water be added, a violent action is exerted, the acid is decomposed with rapidity, copious red fumes are disengaged, and the temperature rises. The tin is so highly oxidated, that it does not pass into a state of solution, but forms a white powder, in which there are even no traces of nitric acid, and which is therefore a pure oxide. If the acid be more largely diluted, as with three or four parts of water, and the tin be added successively in small quantities, the temperature being kept low, the action is more moderate, the metal is less highly oxidated: it is then capable of combining with the acid, and a solution of nitrate of tin is formed.

In the solutions of tin in nitric acid, the metal exists in different degrees of oxidation, according to the strength of the acid, the temperature which has been applied, or the proportions of tin and acid used. Such is the avidity, too, of this metal to oxygen, that in all these cases of the action of nitric acid, whether concentrated or diluted, part of the water is decomposed, and hence a portion of nitrate of ammonia is formed, the hydrogen of the decomposed water being presented in its nascent state to the nitrogen which is evolved from the decomposition of the acid, and forming

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* Fourcroy's System, vol. vi. p. 58.

ammonia, with which part of the undecomposed acid combines. The ammonia can be discovered by adding lime, which soon produces the pungent ammoniacal smell.

The solution of nitrate of tin is not permanent: the metal continues to attract oxygen from the acid, until it become so highly oxidated as not to remain soluble. The same change is produced by heating the solution; a precipitate being deposited.

The action of muriatic acid on tin affords some important results. The metal is dissolved slowly in the cold, and is acted on more rapidly when heat is applied, the tin receiving oxygen from the water, and the oxide combining with the acid. In the cold the solution is accelerated, according to Berard, by exposing the metal alternately to the acid and the air. It has often been observed, that the hydrogen gas disengaged during this solution has a fœtid smell; and this, approaching to the arsenical odour, has been ascribed to the presence of arsenic, which the hydrogen holds in solution: according to the observation of Proust, the arsenic is deposited on the sides of the vessel when this hydrogen gas is burnt *. With regard to this, however, there is some doubt; as the experiments of Bayen, undertaken with the view of determining, whether the prejudice that has long prevailed, of tin containing arsenic, is well founded, establish the conclusion, that in the tin of commerce there is usually no appreciable quantity of arsenic, and that, when it can be discovered, it is extremely minute, never exceeding one grain, and often not half a grain, in an ounce †,—a quantity incapable of accounting for the odour of the hydrogen gas, and the appearance observed by Proust. The black powder which is often deposited in dissolving tin in muriatic acid, is oxide of copper.

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* Journal de Physique, tom. li. p. 175.

† Opuscules Chimiques, tom. ii. p. 274, 411.

The solution of muriate of tin is of a yellowish colour. By evaporation it may be crystallized in needle-like crystals, which are deliquescent. In dissolving in distilled water, according to A. Berthollet, it is decomposed, a precipitate being formed of sub-muriate of tin, while part of the salt, with an excess of acid, remains in solution, both the part dissolved and the part precipitated being in the same state of oxidation. A similar precipitate is produced by the alkalis, (when they are not added in excess, for, in this case, part of the precipitate is dissolved), and from this precipitate a portion of acid may be abstracted by repeatedly washing it with water, but the whole cannot be removed *.

The oxide of tin in this combination, has a great tendency to combine with a large proportion of oxygen. It absorbs the oxygen of atmospheric air, and its solution is capable of de-oxidating a number of substances. If added to the solutions of other metals, it attracts part of the oxygen of the metal dissolved, while it passes itself to the maximum of oxidation, and produces precipitates composed of the oxides of the two metals. Thus, mixed with a solution of gold, it forms a purple precipitate; with a solution of copper, a white precipitate; and with other metallic salts, precipitates of various colours: the solution of nitrate of mercury is completely reduced by it: it attracts, too, the oxygen from metallic oxides, and from sulphurous, nitric, and oxymuriatic acids.

By such processes, a muriate of tin is formed at a higher degree of oxidation, and which differs much in its properties from the other. The process which has been long employed to form this, is to expose to heat in a retort, connected with a receiver, a mixture of an amalgam of five parts of tin and one of quicksilver, with an equal weight of corrosive muriate of mercury; the oxygen and the mu-

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* Chemical Statics, vol. ii. p. 475.

riatic acid of the latter are transferred to the tin, and the product distilled by the heat applied, condenses in the receiver, and forms a dense liquid, which exhales vapours on exposure to the atmosphere. To the older chemists this was known by the name of the Fuming Liquor of Libavius. Pelletier gave another process for preparing it,—passing a current of oxymuriatic acid through a solution of muriate of tin, and expelling the excess of muriatic acid by the application of heat *. Or if tin be heated gently in oxymuriatic acid gas, the gas is condensed, with the phenomena of combustion, and the product is a liquid the same as the liquor of Libavius.

This preparation obtained by the old process is in a highly concentrated state. A series of experiments were made upon it by Adet †. It owes its fuming property, he found, to its volatility when it is free from water; the vapours being produced by its combination with the humidity of the atmosphere; and these vapours, when condensed, form even slender crystals. Its odour is acrid. It dissolves in water with a hissing noise, and the production of an elastic fluid. When combined with about a third of its weight of water, it forms a solid mass, which is capable of being fused by heat, and congealed by cold. It is sublimed by a gentle heat without decomposition.

Adet and Pelletier supposed, that this substance is a compound of oxide of tin with oxymuriatic acid. It is rather to be regarded, as Proust observed, as a compound of tin highly oxidated with muriatic acid. According to Berzelius, it is composed of 42.125 of muriatic acid, and 57.875 of peroxide of tin ‡. Considering this compound as a chloride of tin, it consists, according to Dr J. Davy's analysis of it, of 42.1 of tin, and 57.9 of chlorine. The

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* Memoires de Chimie, tom. i. p. 588.

† Annales de Chimie, tom. i.

‡ Annales de Chimie et Physique, tom. v. p. 152.

proto-muriate of tin is, according to the same doctrine, a compound with a smaller proportion of chlorine: the proportions assigned are 62.22 of tin, and 37.78 of chlorine. It is formed not only by evaporation of the common solution of the muriate to dryness and fusion, but also by heating an amalgam of tin and calomel, and it is converted into the other compound when it is heated in oxymuriatic gas. It is fusible, and of a grey colour, with a resinous lustre and fracture *.

Nitro-muriatic acid dissolves tin with rapidity. When the acid is undiluted, the metal attracts so much oxygen, that a great part of the oxide falls down. To moderate the action, small pieces of tin are added at a time; one is allowed to dissolve before the other is added, and the vessel in which the solution is performed is kept surrounded with cold water. The acid thus takes up half its weight of the metal. The solution is transparent and brown coloured: it becomes of the consistence of a jelly, and at length so firm, that it can be cut with a knife. When it remains fluid, it is rendered of a thick consistence, by the addition of half its weight of water, which decomposes the solution, and precipitates a quantity of oxide that remains dispersed through the fluid. The transparency of the jelly is thus changed, and it becomes opalescent. If the fluid solution be heated, an effervescence is excited from the farther action of the metal on the acid: it loses colour, and on cooling is transparent and gelatinous. The solution of tin in nitro-muriatic acid is of great utility in the art of dyeing, as a mordant; the oxide precipitated from it serving as a bond of union between the colouring matter and the stuff: it also heightens several colours, especially scarlet from cochineal. In using it, much difficulty is experienced from the uncertainty of obtaining it in an uniform state, the tin being so susceptible of various degrees

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* Philosophical Transactions, 1812.

of oxidation; and the different muriates that are formed also containing an excess of acid, which alters the shade of colour.

The action of the other acids on tin, affords less important results. Phosphoric acid has scarcely any effect upon it. When a solution of phosphate of soda is added to a solution of muriate of tin, a phosphate of tin is precipitated. By a similar process, fluate and borate of tin may be formed: they are both insoluble in water.

Iodine and tin combine when they are heated together; the compound is very fusible, of an orange-yellow colour: it is decomposed by water; hydriodic acid and oxide of tin are formed, which remain in combination if the quantity of water is not large, and form a silky-like salt of a yellow colour; if the water has been added in large quantity, the hydriodic acid remains in solution, and the oxide of tin is precipitated *.

The alkalis are capable of combining with oxide of tin. When an alkaline solution is added to muriate of tin, if the alkali is added in excess, the precipitate is re-dissolved, and an appearance somewhat singular, that of a kind of metallic arborescence or vegetation, is formed after some time, as Proust observed. This, as Berthollet *junior* remarked, is owing to the affinity of the alkali being greatest to the oxide which is at the maximum of oxidation: in consequence of this, it causes one part of the oxide, which had been precipitated from the muriate, and which it had dissolved, to pass to this state of high oxidation, while the other part returns nearly to the metallic state; and, as the change goes on slowly, its particles, in uniting, assume the peculiar arrangement which gives rise to the appearance observed †. The triple salts formed by adding the alkalis in excess to the solutions of tin, are capable of crystalliz-

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* Gay Lussac, Annales de Chimie, tom. xci. p. 26.

† Chemical Statics, vol. ii. p. 477.

ing. That of muriate of tin and potash, is in the form of a rhomboidal prism, as is also the muriate of tin and ammonia, and the muriate of tin and barytes. The muriate of tin and soda, as well as the muriate of tin and strontites, crystallize in slender acicular crystals. The muriate of tin and lime is deliquescent *.

The alkalis appear to be capable of dissolving the oxides of tin, independent of the presence of any acid; and form even concentrated solutions. In conformity to the law generally observed in the relation of the alkalis to metallic oxides, their attraction is more powerful to the oxide as the degree of oxidation is greater. The compound of oxide of tin and potash, Proust observes, crystallizes in lenticular crystals. It is rather with the hydrated oxide than the pure oxide that the alkali combines, for although the combination is easily established with the oxide in its humid state, it cannot be easily formed after it has been ignited, and the compound is decomposed, as Berzelius remarked, by exposure to a red heat, so that the alkali may be removed by water.

Tin and its oxides decompose several of the neutral salts, especially the ammoniacal salts; the ammonia being disengaged on the application of heat, with hydrogen gas, when metallic tin is used. It deflagrates with the nitrates; and, from its affinity to oxygen, it decomposes the sulphates, converting them into sulphurets.

Tin combines with sulphur by fusion. The compound is less fusible than the metal; is of a dark grey colour, retains the metallic splendour, and crystallizes in cubes.

Sulphur, heated with oxide of tin, forms a compound of a golden colour, and highly beautiful appearance, named Aurum Musivum, or Mosaic Gold, which has been used for ornamental purposes. Different methods have been employed to obtain this compound. The following is the

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* Chemical Statics, vol. ii. p. 478.

process given by Woulfe: Twelve parts of tin are melted in a crucible, and three parts of mercury added to it. The amalgamation of the two metals is completed by rubbing the mass to a fine powder. It is then intimately mixed by trituration, with 7 parts of flowers of sulphur, and 3 parts of muriate of ammonia. The mixture is put into a matrass, of which it fills one half, and exposed to heat as long as any white vapours are disengaged. On increasing the heat a little, sulphuret of mercury, with a portion of muriate of tin, sublimes, and the aurum musivum remains at the bottom of the matrass. If the process has been properly conducted, it is of a flaky texture, and rich yellow colour: if too much heat has been applied, common sulphuret of tin is formed.

The theory of the formation of this compound was thus illustrated by Pelletier *. The trituration of the mercury with the tin, serves principally to divide the latter metal. When the mixture of the amalgam with the sulphur and muriate of ammonia is heated, the muriatic acid causes the tin to be oxidated by the water present: a disengagement of hydrogen therefore takes place: the oxide of tin combines with the muriatic acid, and the ammonia combining with part of the sulphur, forms sulphuret of ammonia, which produces the white fumes that are disengaged. By the heat being a little increased towards the end of the operation, the muriate of tin is decomposed, the muriatic acid is expelled, and the oxide of tin, attracting a portion of sulphur, forms the aurum musivum.

Other processes, more simple, were proposed by Pelletier. If 600 grains of sulphur be added to 600 grains of tin, dissolved in 4 ounces of muriatic acid, and the fluid be evaporated until it remain concrete; on exposing this mass to heat, muriate of tin, with a little sulphur, is sublimed, and the residuum is aurum musivum. It is ob-

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* Memoires de Chimie, tom. ii. p. 89.

tained likewise, by exposing to heat mixtures of sulphuret of tin, with corrosive muriate of mercury, or with red oxide of mercury, or a mixture of oxide of tin with an equal part of sulphur; or it may be formed in the humid way, by adding a solution of sulphuret of potash to a solution of muriate or nitrate of tin: the precipitate is a compound of oxide of tin and sulphur: it is of a yellow colour, and, if heated alone, or in mixture with half its weight of muriate of ammonia, and one-fourth its weight of sulphur, is converted into the mosaic gold *.

Pelletier advanced the opinion, that the tin exists in this combination in a high degree of oxidation. According to Proust it is at the *minimum*, as he found, that when it is formed by exposing to heat a mixture of sulphur and oxide of tin at the *maximum*, there is a disengagement of sulphurous acid gas, proving an abstraction of oxygen from the oxide; that it still remains oxidated, he supposed to be proved by the experiment, that when decomposed by heat, sulphurous acid is expelled, and sulphuret of tin remains †. It appears, however, that this result is incorrect; no sulphurous acid is disengaged, sulphur only is expelled, as Dr J. Davy found, and the grey sulphuret of tin remains. It can be formed too, as Pelletier himself found, by heating cinnabar with tin; and as cinnabar is a pure sulphuret, the product of its action on the tin must be the same. It is therefore a sulphuret of tin, differing from the grey sulphuret in containing a larger proportion of sulphur. It is difficult to determine the proportions of either by direct experiment. The sulphuret formed by the direct action of tin and sulphur is liable to be variable, from the volatilization of part of the sulphur in its formation; but when this is obviated by heating the product a second time with sulphur, it appears, from the increase of

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* Pelletier, Memoires de Chimie, tom. ii. p. 92-9.

† Nicholson's Journal, vol. xiv. p. 40.

weight which the metal gains, according to the experiments of Dr J. Davy, to be composed of 100 of tin with 27.3 of sulphur. Berzelius had assigned the proportions of 100 with 27.234, or 79.6 with 21.4. He found it difficult to determine the proportions of the super-sulphuret with perfect precision, as it is not easy to obtain it altogether pure; those he found by experiment were 100 of tin with 52.3; and as this quantity of sulphur is not far from twice that in the other compound, it may be inferred, he remarked, from the law of multiple proportions, that the exact quantity will be twice that in the other [*]. Dr J. Davy assigned, from the analysis of the super-sulphuret, by converting it by heat into the sulphuret, the proportions of 100 with 56.25 [†]. Berzelius supposed the existence also of an intermediate sulphuret, but this rested on the incorrect assumption of an intermediate oxide between the protoxide and peroxide.

The alkaline sulphurets combine with tin by fusion; the compound is in part soluble in water: on adding an acid to the solution, a precipitate is thrown down of tin, probably oxidated, combined with sulphuretted hydrogen.

Tin is tarnished by sulphuretted hydrogen gas. The alkaline hydro-sulphurets form precipitates with its saline solutions. If the metal be at the *minimum* of oxidation, the colour of the precipitate is a deep brown: if at the *maximum*, it is of a golden yellow colour. In intermediate degrees of oxidation, various shades between brown and yellow are produced.

Tin combines with phosphorus; the compound being formed by throwing small pieces of phosphorus on melted tin: it contains, in 100 parts, from 15 to 20 of phosphorus. It is of a silver-white colour, and a foliated texture: it is soft, so that it can be cut with a knife; and it can also

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[*] Nicholson's Journal, vol. xxxv. p. 162.

[†] Philosophical Transactions, 1812.

be flattened under the hammer. It inflames when thrown on burning fuel. This compound can be also formed, by fusing in a crucible tin-filings and concrete phosphoric acid, one part of the tin combining with the oxygen of the acid, the other with the phosphorus.

Tin combines with the greater number of the metals: several of its alloys are in common use; and the principal consumption of it, indeed, is in the formation of these alloys. An opinion had generally prevailed, that it destroys the ductility of gold, when combined with it even in a very minute proportion. Mr Alchorne shewed that this is an error; as gold may be alloyed with even $\frac{1}{24}$ of tin, and still remain sufficiently ductile to be laminated, and to be drawn into fine wire. Tillet, from a repetition of his experiments, concluded, that gold alloyed with tin acquires rigidity and hardness, and that, though it may be beat out, it cannot be annealed so as to bear extension to any great degree of thinness *. Mr Hatchet, however, in his researches on the alloys of gold, confirmed the conclusion of Alchorne; and the common opinion, as well as the results of Tillet's experiments, must have arisen from the presence of lead, antimony, bismuth, or zinc, in the tin of commerce, any of these metals rendering gold very brittle. The alloy of gold and tin has, however, no valuable quality: the colour is pale, and when the tin amounts to one tenth, the ductility of the gold is considerably impaired, especially at a high temperature. The tin is not easily abstracted from the gold. Tin has been supposed to be equally destructive of the ductility of silver as of gold; but on this subject accurate experiments are wanting. The alloy is hard, its colour is bluish-grey, and it has a specific gravity greater than the mean specific gravity of its ingredients. With platina and tin a compound is formed, brittle and very fusible when the proportions are equal parts; but

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* Nicholson's Journal, 4to, vol. ii. p. 140.

when one part of platina is combined with 12 parts of tin, the alloy is more ductile. Quicksilver dissolves tin readily, amalgams being formed of various degrees of consistence according to the proportions. With four parts of tin, and one of quicksilver, it is solid, and capable of crystallizing.

A series of alloys is formed from the combination of copper with tin, sufficiently important to require more particular notice. The combination appears to have a tendency to form in certain proportions, regulated by the specific gravities and fusibilities of the metals; for, when kept in fusion, and allowed to cool without agitation, two alloys are formed, the under part of the mass being copper with a small portion of tin, and the upper part tin with a small proportion of copper, while between these there is probably a gradation. By agitation the separation is counteracted. The general effect is, that tin lessens the ductility of copper, while it renders it more hard, rigid, and sonorous; these qualities are possessed in various degrees by the different alloys, according to their proportions, the hardness and brittleness being greater as the tin predominates. The density of the compound is also always greater than the mean density; the contraction from the combination being so great, according to an experiment by Dr Pearson, as one-eighth. The principal of these alloys are bronze, bell-metal, the metal of which pieces of artillery are cast, and that which has been used for the mirrors of reflecting telescopes. Bronze is the one in which the proportion of tin is least, not exceeding 10 or 12 parts in 100. It is of a greyish yellow colour, harder than copper, less liable to rust, and more fusible, so as to run thin, and be easily cast in a mould. Hence its use in the casting of statues. The metal that pieces of artillery are cast from, is of similar composition. It appears that an alloy similar to bronze was much in use among the ancients: swords, darts, and other warlike instruments, were formed of it, as were also various utensils. According to Dr Pearson's experiments made on various ancient instruments of this kind, the alloy appears to have consisted of about eight or nine parts of copper, with one of tin; and, as he remarks, this still affords the best substitute for iron or steel: while the art, therefore, of manufacturing iron was imperfectly known, and difficult to be practised, it must have been much used *. This analysis has since been confirmed by Klaproth, who found antique swords, knives, rings, and other instruments, to be composed of from 87 to 89 of copper, with 11 to 13 of tin †. The hardness of this alloy observed in ancient arms, had even given rise to an opinion, that the ancients were acquainted with a method of hardening copper, which had been lost. Of this alloy medals and coins were also often formed, as appears from the experiments of Dizé on several Roman, Greek, and Gallic coins ‡; and mirrors, cups, and vases, were of a similar composition, containing, according to Klaproth, a larger proportion of tin. When the proportion of tin is increased, the alloy is rendered more brittle, and also highly sonorous; hence bell-metal is a compound of this kind: the proportion of tin varies from one-third to one-fifth of the weight of the copper, according to the size of the bell, and the sound required. The Chinese Gong-Metal, which is so highly sonorous, is composed of 80 of copper, with 20 of tin ||. When the proportion of tin is greater, an alloy is formed of a white colour, and which, from the closeness of its texture, and its susceptibility of a fine polish, exceeds any metal in the property of reflecting light: hence its adaptation to the purpose for which it is used,—the forming the speculum of reflecting telescopes:

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* Philosophical Transactions, 1796, p. 595.

† Nicholson's Journal, vol. xxvi. p. 86.

‡ Journal de Physique, 1790, p. 272.

|| Annals of Philosophy, vol. ii. p. 209.

it has also the advantage of not being liable to tarnish on exposure to the air. The proportion in which these qualities are best attained, appeared, from the experiments of Mudge, to be a little less than one part of tin, with two parts of copper *. Mr Edwards, by an extensive series of experiments on the proportions of these metals, and the effects of different additions, succeeded in forming alloys superior in brightness to those that had been before used. That which he preferred, was composed of 32 ounces of copper, with 15 or 16 ounces of tin, to which were added brass, arsenic, and silver, of each one ounce; the copper and the tin being melted in separate crucibles, when in fusion the one being added to the other, and the composition when well stirred being poured into cold water: the other metals are added in a second fusion: the arsenic appears to give a greater degree of density and compactness to the alloy, the brass more tenacity, and the silver adds to the whiteness †. According to the still more recent experiments of Mr Little ‡, the silver renders the alloy too soft to admit of a high polish. The composition which he has recommended is 32 parts of bar copper, 4 parts of brass, 16½ parts of tin, and 1¼ of arsenic.

From the affinity between tin and copper, a thin layer of the former can be applied to the surface of the latter; and this practice of tinning is often applied to prevent the erosion or rusting of copper-vessels, and the noxious impregnation which they would communicate to liquors kept in them. The surface of the copper is polished so as to be quite bright: sal ammoniac is applied to it when hot, by which the oxidation appears to be prevented; or pitch is sometimes used for the same purpose; the melted tin, or,

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* Philosophical Transactions, vol. lxvii.

† Nicholson's Journal, 4to, vol. iii. p. 490.

‡ Transactions of the Irish Academy, vol. x. or Nicholson's Journal, vol. xvi. p. 55.

what is often substituted, on account of its hardness being greater than that of pure tin, an alloy of tin and lead, is applied to the surface of the copper, to which it adheres. Klaproth has observed, that an alloy of copper and tin, similar to bronze, would be preferable to copper vessels used in the preparation of food, as being harder, and therefore less liable to erosion, and also less liable to oxidation.

Tin and iron may be combined by fusion. In this, as in many other metallic combinations, two alloys are established, differing in the proportions, in the different parts of the same mass. The one, that in which a small proportion of iron, about $\frac{1}{22}$, is combined with tin, is malleable, harder than tin, but still sufficiently soft to be cut by the knife; the other, in which iron is alloyed with a smaller portion of tin, is much harder, is slightly malleable, and not easily fused. On the affinity between iron and tin, is founded the art of forming tinned iron, or what in this country is named White Iron. Thin plates of malleable iron cleaned, are dipt into a vessel of melted tin, the surface of which is protected from oxidation, by a thin layer of melted tallow: the tin unites with the iron at each surface: it is doubtful whether it penetrates the entire substance of the iron or not. The iron acquires a white colour; is rendered less liable to rust; its ductility is little impaired: hence the plates can be easily bent, and from the alloy of tin at the surface can be also easily soldered.

Tin and lead differing little in fusibility, can be united in all proportions. The lead, by an addition of tin, acquires greater hardness. This alloy forms the compound metal named Pewter, into the composition of which zinc and copper sometimes also enter. The alloy of equal parts of tin and lead, forms the soft solder used in soldering tinned iron plates. When the alloy of tin and lead is digested in acetic, or even in muriatic acid, none of the lead is dissolved, but only the tin: from this probably the use of pewter vessels is more safe. In nitric acid both metals are dissolved, the lead in largest proportion.

The amalgam of tin is used in covering the backs of glass mirrors. Tin in thin leaf is laid on a smooth stone table; and quicksilver being poured over it, it is extended over the surface by a rubber of cloth: the surface of the tin leaf becomes slightly oxidated, and this film of oxide is removed by the rubber. More quicksilver is then poured over the tin, so as to cover it to the thickness of a line. The glass is applied in a horizontal direction at one end of the table, and is pushed forward so as to remove before it the oxide at the surface of the amalgam. Weights are placed on it, to force out the superfluous quicksilver, and a thin crust of amalgam adheres to the glass, giving the property of reflecting light.

It is principally in the formation of these alloys that tin is used. Its oxides are employed in enamelling and in polishing the metals; and its solution in nitro-muriatic acid, is used as a mordant in the art of dyeing.

CHAP. XIII.

ZINC.

This metal was unknown to the ancients, though they were acquainted with one of its ores, calamine, and the effect which it has of converting copper into brass. It appears to have been discovered during the researches of Alchemy. Swab and Margraaf gave the process by which it may be extracted from its ores by distillation. The method of extracting it has also been long known in India and China; the metal brought from these countries, under the name of Tutenag, being principally zinc *.

This has usually been ranked among those metals, which, from their imperfect ductility and malleability, have been named Semi-metals. It was known, however, that, by uniform pressure, it might be extended into thin plates; and more lately, it has been discovered, that, at a certain temperature, it has so much malleability and ductility, that it can be laminated, and drawn into wire. The temperature at which it possesses these properties, is between 210° and 300° of Fahrenheit; and by keeping it in an oven at this heat, it may be extended without difficulty. By being annealed, it retains this tenacity so as to be easily bent †. At a higher temperature, it is brittle, so as to fall to pieces under the hammer.

Zinc is of a white colour, with a shade of blue, and, in a fresh fracture, has considerable lustre. It is hard, so that, although it can be scratched, it is not cut by a knife. Its texture is striated. Its specific gravity is 7.190.

There are two principal ores of zinc, what have been named Calamine and Blende; the first an oxide, frequently with a portion of carbonic acid; the other a sulphuret. From either of these it was found difficult to extract zinc, owing to the circumstance that it is volatilized by heat. On this, however, was at length founded the process of obtaining it by distillation. Calamine is the ore usually wrought. Being pounded, it is calcined so as to expel any carbonic acid; it is then mixed with charcoal: the mixture is put into conical pots, closed at the head; an open iron tube being fixed in each, reaching nearly to the top, and descending through the bottom, passing through the floor of the furnace, and terminating in a vessel of water. Heat is applied around the pots, so as to reduce and volatilize

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* Bergman's Essays, vol. ii. p. 311.

† Nicholson's Journal, vol. xi. p. 304.

the zinc; the vapours of which, passing through the tube, are condensed in the water. When the extraction of zinc from blende is attempted, it is volatilized in a furnace, the vapours being received in a bed of charcoal.

This metal melts a little before ignition, or nearly at 700° of Fahrenheit. When heated near to its melting point, it is so brittle, that a blow of a hammer reduces it to powder. Its crystallization is difficult. Pelletier obtained it in flattened hexaedral prisms *. In close vessels, by an increase of heat, it is volatilized without change.

When zinc is melted in contact with the air, its surface becomes covered with a grey powder, which is an imperfect oxide. If the temperature is raised to ignition, or a little higher, it burns with a bright flame, at first of a greenish or yellowish colour, but which, as the heat is increased, becomes of a dazzling white: a white oxide is formed, which is carried up in light flocculi, which have been termed the Flowers of Zinc, or Philosopher's Wool. The apparent volatilization of the oxide is owing to the volatility of the metal, and the current of air, as by itself it is not volatile. It remains fixed in a crucible in a very strong heat. When urged by an intense heat, it is vitrified; the glass having a beautiful yellow colour. In this operation, the oxide loses a little oxygen. It is not completely reduced, unless by exposure to heat with substances capable of affording carbon, which attracts its oxygen. Zinc, in its vivid combustion, gains 17 parts by weight in 100; but there is a loss, from part being carried off by the rapid current of air. According to Proust, the white oxide, formed by this combustion, consists of 80 parts of zinc, and 20 of oxygen, or 100 with 25 †. Clement and Desormes stated its proportions at 82 of zinc, and 18 of oxygen, or 100 with 22: after having been urged by a strong heat,

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* Mémoires de Chimie, tom. i. p. 58.

† Annales de Chimie, tom. xxxv.

until it acquire a yellow colour, it contains only about 11 of oxygen *. According to Vauquelin, the oxide of zinc, which exists in some of its saline combinations, as the sulphate or nitrate, contains 0.21 of oxygen †. The existence of the lower degree of oxidation has been denied, and that of one oxide only maintained. Gay Lussac and Berzelius assign to it precisely the same proportions, 80.39 and 19.61, or 100 with 24.4, which differ little from those of Proust. Dr Thomson has, from experiment, inferred that of 100 of metal with 24.16 of oxygen ‡.

Zinc is little acted upon by water, at the common temperature of the atmosphere; it is oxidated, however, and a hydrate formed, as Guyton and Vauquelin have shewn. At ignition the water is rapidly decomposed, the metal attracting its oxygen, and a large quantity of hydrogen gas being disengaged. This experiment is difficult to make, as the metal is volatilized by the necessary degree of heat.

Zinc is oxidated and dissolved by the greater number of the acids.

The concentrated sulphuric acid requires the assistance of heat, and sulphurous acid gas is expelled. When diluted with 3 or 4 parts of water, the oxidation and solution go on rapidly in the cold; the metal decomposing the water. A portion of a black powder separates during the solution, which has been generally supposed to be carbon or plumbago that had been combined with the zinc. According to Proust, it is a mixture of arsenic, lead, and copper. According to Vogel, it consists of charcoal, iron, and lead. When the solution is filtered, it is colourless, and, when concentrated by evaporation, affords crystals, which are slender prisms of four sides, acuminated by four

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* Annales de Chimie, tom. xlii. † Ibid. tom. xxviii. p. 50.

‡ Annales de Chimie, tom. lxxx. lxxxi. Annals of Philosophy, vol. ii. p. 410.

planes. This salt, the sulphate of zinc, has a styptic taste; is soluble in three times its weight of water at the temperature of 60°; and undergoes the watery fusion, when moderately heated. According to Kirwan, it consists, in its crystallized state, of 40 of oxide of zinc, 20.5 of acid, and 39 of water. Mr Smithson gives its composition, when freed from water, at 50 of oxide, and 50 of acid. According to Berzelius, it consists of 32.585 of oxide of zinc, 30.965 of sulphuric acid, and 36.45 of water.

Sulphate of zinc is prepared in the large way, from some varieties of the native sulphuret. This ore is roasted, moistened, and exposed to the atmosphere: the sulphur attracts oxygen, and is converted into sulphuric acid: the metal is oxidated, and combines with the acid. The sulphate of zinc is extracted by lixiviation: the solution is evaporated to dryness, and run into moulds. The salt is in hard masses, of a granulated texture, and a yellowish white colour. This is the white vitriol of commerce. It generally contains a small portion of iron, and sometimes of lead.

Sulphurous acid dissolves zinc, sulphuretted hydrogen gas being formed from the decomposition both of the acid and of the water. On exposure to the air, it deposites needle-like crystals, which, according to Fourcroy and Vauquelin, are sulphuretted sulphite of zinc. By dissolving oxide of zinc in sulphurous acid, the pure sulphite is obtained. It is soluble and crystallizable.

Nitric acid acts on zinc with great violence; is decomposed with a rapid effervescence; and nitric oxide, and nitrous oxide gases, with nitrous acid vapour, are disengaged. The nitrate of zinc is best obtained by using a dilute acid: by evaporation and cooling, it crystallizes in hexaedral prisms, acuminated by four planes. These are deliquescent, soluble in water and alkohol: they are decomposed by the gentlest heat, and detonate on ignited fuel.

Muriatic acid dissolves zinc with rapidity: the water mixed with the acid being decomposed, and hydrogen being disengaged. The solution does not afford crystals by evaporation, but becomes gelatinous. By raising the heat, this is partially decomposed; part of the muriatic acid is expelled, and another part of the muriate of zinc is sublimed, and condenses in a mass, consisting of a congeries of prisms. A solid product is also obtained by the combustion of zinc in oxymuriatic gas, which is soft, fusible, and is not volatile at a red heat. The same product is obtained by heating zinc with corrosive muriate of mercury. Considering it as a chloride, it consists, according to Dr J. Davy's analysis of it, of 50 of zinc and 50 of chlorine.

Phosphoric acid, in its liquid state, dissolves zinc with a disengagement of hydrogen gas, forming a solution which does not crystallize, but by evaporation becomes gelatinous, and by a strong heat may be melted. The concrete phosphoric acid, heated with zinc-filings, is decomposed. Fluoric acid also dissolves zinc, hydrogen gas being evolved. Boracic acid, digested with it, becomes milky; and an insoluble borate of zinc is precipitated on adding a solution of borax to a solution of muriate or nitrate of zinc. Carbonic acid, combined with water, dissolves a small quantity of zinc, and dissolves still more readily the oxide of zinc: when the liquid is exposed to the air, a thin iridescent pellicle forms on its surface, probably from the escape of the acid.

Iodine acts on zinc when a moderate heat is applied; the compound formed is colourless, melts easily, volatilizes, and condenses in acicular quadrangular prisms; it is very soluble in water, and deliquesces rapidly; the solution is uncrystallizable and slightly acid; the alkalis precipitate oxide of zinc from it, and sulphuric acid disengages hydriodic acid, with a portion of iodine from the acid being decomposed. The solution, therefore, contains hydriodate of zinc. 100 of iodine, according to Gay Lussac, combine with 26.225 of zinc, and 100 of hydriodic acid, with 32.352 of oxide of zinc *.

The salts of zinc are decomposed by the alkalis; the oxide being precipitated. If a larger quantity of alkali be added, the precipitate is re-dissolved. The alkalis likewise dissolve the white oxide of zinc in its pure state. On this solubility of oxide of zinc in the alkalis, Vauquelin founded a method, to be immediately stated, of analysing brass, which is a compound of zinc and copper. The fixed alkalis act even on metallic zinc, and promote its oxidation by the oxygen which water holds dissolved, or by the decomposition of water itself, as a little hydrogen gas is observed to be disengaged. Liquid ammonia exerts on metallic zinc a similar action.

From the strong affinity which zinc exerts to oxygen, it decomposes the greater number of the metallic salts, deoxidating either partially or completely the oxides which enter into their composition.

Zinc has been said to be soluble in small proportion in hydrogen gas, so that when water is decomposed by it, aided by the affinity of an acid, the hydrogen disengaged, holds a small portion of the metal dissolved, which it deposites in burning in the state of a white oxide: but the accuracy of this statement is doubful.

Carbon does not combine with zinc; yet zinc, in the state in which it is met with in commerce, deposites, while dissolving in an acid, a quantity of a black powder, in which carbon has been supposed to be contained; it appears, however, to consist chiefly of copper and lead †.

Zinc cannot easily be combined with sulphur. When they are exposed together to heat, the sulphur is volatilized, and no portion of it combines with the zinc; yet their combination exists in nature, the ore of zinc, named

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* Annales de Chimie, tom. xci. p. 25. 66.

† Ibid. tom. xxxv. p. 52.

Blende, being a sulphuret. According to Proust, if oxide of zinc be heated with an equal weight of sulphur, the oxide is decomposed, sulphurous acid is disengaged, and sulphuret of zinc is formed. And according to some observations, on heating zinc with sulphur, excluding the air, a sulphuret of zinc of a yellowish white colour is obtained *. Blende always contains iron, and frequently other ingredients; but abstracting these, and considering it as sulphuret of zinc, Dr Thomson inferred, from a careful analysis, that it is composed of 67.19 of zinc, and 32.81 of sulphur, or 100 with 48.84 †. The oxide of zinc can be combined with sulphur by fusion, and a compound is formed of a brown colour, which, by sublimation, affords needle-like crystals of a yellow colour. The alkaline sulphurets do not dissolve the metal. Sulphuretted hydrogen, added to the solutions of its salts, throws down a white precipitate, probably a hydro-sulphuretted oxide of zinc.

Zinc may be combined with phosphorus, by projecting small pieces of phosphorus on the metal melted in a crucible, a little resin being added to prevent its oxidation. The phosphuret of zinc is of a white colour, with a shade of bluish-grey; has metallic lustre; is a little malleable; and burns when exposed to heat. Phosphorus appears also to combine with oxide of zinc: when zinc and phosphorus are exposed to heat in a retort, a red-coloured sublimate is formed, and also a sublimate consisting of needle-like crystals, with metallic lustre, and of a bluish colour, both of which Pelletier regarded as compounds of phosphorus with oxide of zinc. When phosphoric acid and zinc, either with or without a little charcoal, are heated together, needle-like crystals are sublimed, of a silvery

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* Journal des Mines, No. 126. 129.

† Annals of Philosophy, vol. iv. p. 94.

white colour, which he also considered as a phosphuretted oxide of zinc. It is highly inflammable *.

Zinc combines with a number of the metals. With gold it forms alloys of a pale colour, more hard and brittle as the zinc predominates: that from equal parts of the two metals is of a white colour, receives a fine polish, and does not tarnish. A small portion of zinc is sufficient, as appears from Mr Hatchet's experiments, to destroy the ductility of gold. Keeping them in fusion in separate crucibles near each other, has even this effect. The ductility of silver is also impaired by zinc. Platina forms with it a hard brittle alloy, of a bluish colour. It combines with quicksilver, either by trituration or applying heat, and forms a kind of granular mass, which, when solid, from a sufficient proportion of zinc, is capable of crystallizing.

The most important alloys of zinc, are those which it forms with copper. The two metals may be united by fusion, but the operation is difficult, from the volatilization or oxidation of the zinc. It is more easily effected by the process named Cementation. This consists in exposing to heat a mixture of calcined calamine, the native oxide of zinc, and charcoal, with granulated copper, or placing in alternate layers the copper, and the mixture of calamine and charcoal; by the heat applied the zinc is reduced, and being volatilized, is applied in the state of vapour to the copper; the combination is thus effected; and the compound can afterwards be combined by fusion, with additional proportions either of copper or zinc.

These alloys differ in their properties according to the proportions: all of them have a rich yellow colour, which is deeper as the copper predominates. Brass is the one which contains the largest quantity of zinc. It is of a fine yellow colour, is more fusible than copper, and is therefore

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* Memoires de Chimie, tom. ii. p. 45.

more easily cast: it is less liable to tarnish or rust from exposure to the air, and it possesses a considerable degree of malleability and ductility, as it can both be beat into thin leaves, and drawn into fine wire: its specific gravity is greater than the mean specific gravity of the two metals. There appear to be two kinds of brass, composed of very different proportions of zinc and copper, and possessed of very different properties. One, the more common variety, according to its analysis by Chaudet, consists of from 62 to 66 of copper, with from 32 to 35 of zinc; the other, which is much more ductile, so as to be valued for the fabrication of those instruments which required hammering, he found composed of 70 of copper, and 30 of zinc. Dr Thomson had made the same observation, and found the difference in proportions greater: the proportion of copper in the ductile brass, which is usually known by the name of Nurenberg or Dutch brass, being twice that in the other. Its superior ductility seems, however, to be in part owing to the purity of the alloy; the common brass usually containing a little lead *. With a larger proportion of copper, other alloys are formed of a deeper colour, inclining to red; such are princes-metal, pinchbeck, and tombac. They are formed by fusing brass with an additional quantity of copper. These alloys are analysed, and the proportions of their constituent parts determined most easily, by the method given by Vauquelin, dissolving the alloy in diluted nitric acid, precipitating the oxides by a solution of potash, and adding an excess of potash, so as to dissolve the oxide of zinc. The oxide of copper which remains, contains, when it has been washed and dried, 65 per cent. of that metal. Another simple mode is to dissolve the alloy in diluted sulphuric acid, and precipitate the copper by zinc †.

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* Annals of Philosophy, vol. xii. p. 19. 125.

† Annales de Chimie, tom. xxviii. p. 40.

Zinc does not easily combine with iron, from the great difference in their fusibilities, and the volatility of the zinc. Yet that they may be combined is proved, by the coating of zinc which iron plates acquire when immersed in melted zinc. With lead it can be united by fusion. The alloy is harder than lead, of a whiter colour, and has some malleability. With tin an alloy is formed, harder than the tin, of a close grain, and having some ductility.

Zinc is principally used in the formation of some of these alloys, particularly those of copper. Since the method of extending it easily into thin plates has been discovered, it has been proposed to employ it as a substitute for lead and copper in roofing houses, in the sheathing of ships, and in forming pipes and cisterns for conveying or containing water. For the last purpose, or for that which has also been proposed, of employing it for vessels for the preparation of food, it is unfit, as, from the report of the Commission of the French chemists, it appears to be easily acted on, even by water, and to be injurious to health *.

CHAP. XIV.

BISMUTH.

THIS metal appears to have been known imperfectly to the alchemists. Pott and Geoffroy distinguished it with accuracy; Rouelle and Darcet submitted it to an experimental investigation; and Bergman undertook a farther examination of its properties and combinations.

Bismuth occurs native, and mineralized by oxygen and

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* Annales de Chimie, tom. lxxxvi. p. 51. 115.

by sulphur. The uses of this metal being very limited, it is scarcely wrought on a large scale. What is used, is generally native bismuth, freed by fusion from the substances with which it is naturally mixed.

It is of a white colour, with a tinge of yellow; its lustre is liable to tarnish from exposure to the air. Its texture is foliated, the plates being large. Its hardness is inferior to that of copper. It is not ductile, and scarcely malleable; for although flattened a little by the hammer, it cannot be reduced to thin plates. Its specific gravity is 9.822.

Bismuth is one of the most fusible of the metals. Its fusing point, according to Lewis, is 460°; according to Irvine, 480°. It is easily crystallized, its crystals being rectangular prisms, or octaedrons. By raising the heat considerably above its melting point, it is volatilized.

If, when in fusion, the air is freely admitted, it is soon covered with a film which increases, and a greenish-grey oxide is formed, the metal increasing in weight about one-twelfth. If it be exposed to a stronger heat, it burns with a small blue flame, and emits vapours, which condense into a yellow powder, in which the metal gains still more weight: the oxide is fused by heat into a glass, transparent, and of a green or yellow colour. A white precipitate is obtained from the solution of bismuth in nitric acid, by the affusion of water, which some have considered as the metal in a higher degree of oxidation; but it is a sub-salt, and when freed from any adhering acid by an alkali, a hydrated oxide. The oxide seems to be obtained most uniform by submitting the metal to the action of nitric acid, evaporating to dryness, and heating to redness. From experiments in this mode, conducted with much care, Lagerhjelm inferred, that the oxide consists of 89.863 of metal, and 10.137 of oxygen, or 100 with 11.28 *. Dr J. Davy, from a similar experiment, assigned the propor-

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* Annals of Philosophy, vol. iv. p. 357.

tion of 100 with 11.1. This oxide, Lagerhjelm found to be of a brick-red colour.

Bismuth is oxidated and dissolved by a number of the acids. The affinities of the acids to the oxide in these combinations are weak, as the greater number of them are decomposed by the affusion of water, the oxide retaining a portion of acid, being precipitated.

Sulphuric acid, when boiled on the metal, is decomposed, sulphurous acid, or even sulphur if the heat is high, being evolved. The residual mass is decomposed by water, which divides the salt into two compounds,—a sub-sulphate that remains insoluble, and a super-sulphate that is dissolved, and affords by evaporation acicular crystals. According to Lagerhjelm, 100 of oxide of bismuth are saturated by 50.71 of sulphuric acid. Sulphurous acid combines with oxide of bismuth, and forms an insoluble compound.

Nitric acid acts with violence on metallic bismuth: very dense red vapours are extricated, and the metal is so highly oxidated, that much of it remains in the form of a white powder uncombined with the acid. When the action is moderated by dilution of the acid, the metal is dissolved. The solution is colourless, and by evaporation affords rhomboidal crystals, which are permanent in the air, and which detonate slightly on burning fuel. The solution, as well as the salt itself, are decomposed by water, a sub-nitrate being precipitated, and a super-nitrate remaining in solution. The colour of this precipitate is a pure white. It was formerly named the Magistery of Bismuth, and has been said to be the substance used as a paint for the complexion, under the name of Pearl White: but it is too acrid for this purpose: the proper pearl white is the tartrate of bismuth, prepared by precipitating the nitrate by tartrate of potash.

Muriatic acid scarcely acts on metallic bismuth, but readily dissolves its oxides. If the solution be evaporated to dryness, and exposed to heat, it sublimes, and condenses in the state of a thick soft mass, which congeals by cold. This was formerly named Butter of Bismuth. It is also obtained in a concentrated state by decomposing corrosive muriate of mercury by bismuth. A similar compound is formed by the action of oxymuriatic acid gas on metallic bismuth; and the metal, if in filings, inflames when projected into the gas. It is neither very fusible nor volatile; it is decomposed by the affusion of water, and oxide or sub-muriate of bismuth is precipitated. Considering it as a chloride, it consists, according to Dr J. Davy's analysis, of 66.4 of bismuth, and 33.6 of chlorine.

The actions of the other acids on bismuth have been little examined. Phosphoric acid combines with the oxide, forming a compound which is insoluble, and which fuses before the blowpipe into a transparent glass. Fluoric acid dissolves the oxide: the taste of the solution is sweetish, and, when it is concentrated by evaporation, it deposites a compound, which is not easily dissolved in water. Boracic acid and carbonic acid may be combined with the oxide by double affinity, and form insoluble compounds.

Iodine acts on bismuth, and forms a substance of a brown colour, insoluble in water.

The salts of bismuth are decomposed by the alkalis, and the precipitates which are thrown down, are dissolved by boiling in a solution of soda or potash, or by digestion with liquid ammonia.

Bismuth does not unite with hydrogen or carbon. It combines with sulphur by fusion, and forms a compound of a grey colour, having metallic lustre. It consists, according to Lagerhjelm, of 100 of metal with 22.52 of sulphur, or 81.62 with 18.38: according to J. Davy, of 100 with 122.3. When melted, and allowed to cool slowly, it concretes into a crystalline mass, composed of tetraedral prisms crossing each other, shining, and often iridescent.

Both the metal and its oxide are acted on by sulphuretted hydrogen. The metal, exposed to the gas, is tarnished; and any of the solutions of bismuth acquires a dark colour, when placed near to any substance emitting this gas. The alkaline sulphurets, or rather sulphuretted hydro-sulphurets, throw down from these solutions very dark-coloured precipitates. By this action, these solutions afford very subtle sympathetic inks.

To phosphorus this metal appears to have a very weak affinity, Pelletier being unable, by the usual processes, to combine them in any sensible quantity.

Bismuth unites with many of the metals, and, in general, communicates brittleness and fusibility; but few of these alloys have been particularly examined, or applied to any use. A very small portion destroys completely the ductility of gold: the merely keeping them in fusion in separate vessels near to each other, has this effect; and the alloy is perfectly brittle when the proportion of bismuth is less than $\frac{1}{1000}$. It also renders the colour of gold very pale. Silver is rendered brittle by an alloy of it, and acquires a yellow colour. The ductility of platina is equally impaired by it: the alloy is fusible, and assumes a purple colour from exposure to the air. With quicksilver bismuth combines easily; the amalgam being of different degrees of consistence, according to the proportions. If the proportion of bismuth be not considerable, the fluidity of the quicksilver is not much diminished: if it be large, as half the weight of the mercury, the amalgam, though at first soft, becomes gradually firm, and is capable of assuming a crystalline arrangement. Copper and bismuth form an alloy of a reddish-white colour, and foliated texture. Iron unites imperfectly with it, though the iron, exposed at a high temperature to its action, is rendered brittle. With lead it unites easily, the lead becoming harder, but at the same time more brittle: the alloy is also more fusible. From the property which bismuth has of increasing the fusibility of lead, as well as of other metals, it has been used in the adulteration of quicksilver. If lead alone were added to the quicksilver, the impurity would be discovered by a diminution of its mobility; but the addition of a little bismuth along with it prevents this, obviously by adding to the fusibility of the compound. This property of bismuth is also well displayed in the formation of what is named the Fusible Metal, which consists of eight parts of bismuth, five of lead, and three of tin. It melts at the temperature of boiling water; and if one part of quicksilver be added, melts at a heat considerably lower. A composition of this kind is used for coating the internal surface of glass globes: it is composed of two of bismuth, one of lead, one of tin, and four of quicksilver; and it fuses with so gentle a heat, that when a little of it is put into a glass globe quite clean and dry, on putting this in warm water, the alloy is melted, and, by revolving the globe, may be spread over its surface, to which it adheres. An alloy, composed of equal parts of tin, bismuth, and mercury, (the tin and bismuth being first melted, and when becoming solid, the quicksilver being added), forms what has been named Mosaic Silver, from its flaky silvery appearance: it is used to give this appearance to plaster casts, paper, &c. The alloy of equal parts of bismuth and tin alone, is so fusible as to melt at 280° of Fahrenheit: when the proportion of tin is larger, it is less fusible; it is at the same time harder than tin, but is brittle. When this alloy is submitted to the action of muriatic acid, the tin is dissolved, with scarcely any of the bismuth. With zinc bismuth does not combine, which is singular, as their fusibilities are not very different. Nickel appears to be capable of uniting with it, forming an alloy brittle, and in brilliant scales. Its combination with cobalt is doubtful, though they may be united by the aid of nickel or arsenic, and occur in this state in nature. It does not unite with manganese.

Bismuth is applied to few important uses. It is principally in the composition of a few metallic alloys that it is employed, particularly to give hardness to lead, and fusibility to some others. Its soft alloy, with tin and antimony, has been proposed to be employed to take impressions of medals, as it gradually acquires greater hardness, and can thus preserve the impression it has taken.

CHAP. XV.

ANTIMONY.

The name Antimony was given by the alchemists to a mineral of a dark grey colour, metallic lustre, and striated texture; which was afterwards discovered to be a compound of a peculiar metal with sulphur. The name is now appropriated to this metal, though, by the older writers, and even at present in commerce, it is applied to the native sulphuret. When used in this last sense, the epithet Crude is generally added to it. No metal has been more the subject of chemical investigation, from its preparations having been long extensively employed in the practice of medicine; and its history, in this point of view, is of considerable importance.

It is from the native sulphuret that the metal is always extracted. The ore is freed from the earthy matter mixed with it, by fusing it in a large earthen pot or crucible covered at the top, and perforated in the bottom, another pot being placed beneath to receive the melted metallic sulphuret; or by melting the ore covered with charcoal powder in the bed of a reverberatory furnace. This forms what is named Crude Antimony, which is massive, striated in its texture, frequently exhibiting distinct prismatic crystals, of a dark grey colour, with metallic lustre. From this the antimony is usually procured, by fusing it with iron-filings. On 32 parts of these heated to redness, 100 parts of the sulphuret are projected, and when the whole is in fusion, 20 parts of nitre are added: the sulphur of the sulphuret is combined partly with the iron, partly with the alkali of the nitre, and the metallic antimony remaining in fusion is poured into conical iron moulds. Or it may be procured probably in a purer state, by exposing the sulphuret for some time to a moderate heat, by which the sulphur is dissipated, and the metal imperfectly oxidated. It is then fused with an equal part of black flux, or of crude tartar: the metal is reduced, and being easily melted is run out.

Antimony, in its pure state, is of a white colour, with a shade of bluish grey: its lustre is metallic; and it is not liable to tarnish much from exposure to the air. Its texture is very distinctly foliated: its hardness is moderate, nearly the same as that of tin: it is quite brittle, incapable of extension, and easily reduced to powder by beating. Its specific gravity is 6.702.

Antimony melts at a little above a red heat, or about 810 of Fahrenheit. When cooled slowly and partially, so that the internal liquid portion can be withdrawn from the external solid crust, the inner surface of the latter is covered with crystals, in the form of single and double tetraedral pyramids. Even when an entire mass of it is consolidated, there frequently appear on the surface stellated spots, from crystallization, and its internal structure is crystalline, being composed of rhomboidal plates, intersecting each other, and divisible in certain directions. When the temperature is raised to a white heat, the antimony sublimes in close vessels.

When the metal is exposed to heat in contact with the air, it is converted into a grey powder, which is an imperfect oxide. This is even more volatile than the metal. If exposed to heat, it sublimes; receiving at the same time a larger portion of oxygen, and condensing in acicular crystals. The same oxide is obtained by exposing the antimony to such a degree of heat, with the admission of air, as is sufficient to volatilize it. It then burns with a feeble flame. The metal is also oxidated, by deflagrating it in filings with twice its weight of nitre, in a crucible heated to ignition; but the oxide prepared in this mode retains a portion of the alkali of the nitre combined with it, which is not abstracted by washing, and which renders it capable of vitrifying.

There is much difficulty in determining the degrees of oxidation of antimony, and very discordant results have been stated with regard to it. Proust endeavoured to shew that antimony is susceptible of only two degrees of oxidation; the one at the *minimum*, containing 18.5 of oxygen in 100 parts, the other at the *maximum*, containing 23. The first is the base of the greater number of the saline combinations of antimony, and is obtained by decomposing the muriate of antimony by water, and boiling the precipitate which that decomposition affords, with a solution of carbonate of potash, to abstract the whole of the acid from the oxide. It is of a greyish white colour, and is fusible by heat, melting into a dense liquid, which on cooling forms an opaque and crystalline mass; it is also volatile, and forms crystals by sublimation. The second is procured by distilling nitric acid from antimony. It is not melted at a red heat, but is volatilized, and condenses in acicular crystals: it is not soluble in water, and is not easily dissolved by acids; it is nearly the same with the oxide obtained by raising antimony to a high temperature in atmospheric air, or deflagrating it with nitre*. Bucholz confirmed these conclusions of Proust.

According to Thenard, there are not less than six oxides

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* Journal de Physique, tom. lv. p. 325.

of antimony capable of being distinguished from each other. The first is of a black colour: it is obtained by precipitating antimony from its solutions by iron or zinc: it contains only 0.02 parts of oxygen. The second is of a chesnut-brown colour: it is obtained by exposing to heat in close vessels, either of the two oxides which are at the highest degrees of oxidation, and which thus lose a portion of their oxygen: it contains 0.16 of oxygen, and is the base of the vitrified oxide, or glass of antimony. The third, containing 0.18 of oxygen, is obtained by the same process, stopping the operation when the orange colour is produced. The fourth, which is yellow, and contains about 0.19 of oxygen, is also obtained by the same process, being the first result of the partial de-oxidation. The fifth, containing 0.20 of oxygen, is white: it is prepared by exposing antimony to such a heat as volatilizes it, the air being admitted; and it exists in several of the saline combinations of the metal, as the tartrate and muriate. The sixth is also of a white colour, and contains 0.32 of oxygen: it is prepared by oxidating antimony by deflagration with nitre: the oxide formed remains in combination with the alkali of the nitre, and the compound is partially soluble in water: on adding an acid to this solution, the oxide is precipitated. By exposing it to heat with various proportions of metallic antimony, it forms the other oxides *. There is no probability that specific degrees of oxidation should be established, with variations in the proportion of oxygen so inconsiderable as the greater number of those assigned in this enumeration.

Berzelius has inferred the existence of four oxides of antimony. The first is formed on the surface of the metal when it is exposed to a warm and humid atmosphere, or when it is placed in water at the positive pole of a voltaic battery; it is a powder of a grey colour, which becomes

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* Annales de Chimie, tom. xxxii. p. 259.

black in drying, without acquiring any lustre, but is resolved by the action of muriatic acid into a higher oxide, and metallic antimony. The second is the first oxide of Proust, and distinguished by its easy fusibility, and forming a yellowish fluid, which consolidates in a radiated mass; heated more strongly it takes fire, and becomes white. The third is obtained by precipitating the solution of antimony in nitro-muriatic acid by water, and exposing the precipitate well washed to strong ignition; it is perfectly white. The fourth is the yellow oxide: it is formed by various processes, such as exposing nitrate or muriate of antimony to a heat sufficient to drive off the acid without igniting the mass, or heating metallie antimony with red oxide of mercury, or with nitre: by the heat of ignition it gives out oxygen, and passes into the white oxide. The following table gives the proportions in these oxides:

	Metal.	Oxygen.	Metal.	Oxygen.
First oxide,	100	4.65	96.326	3.174
Second, -	100	18.60	84.317	15.683
Third, -	100	27.90	78.19	21.810
Fourth, -	100	37.20	72.85	27.150*.

Berzelius corrected the estimate of the composition of the third oxide, to 100 of metal with 24.8 of oxygen †.

Gay Lussac admits the existence of three only of these oxides, rejecting the first, which there is every probability is a mixture of oxide with metallic antimony ‡. And the whole subject must still be considered as not perfectly determined.

The more perfect oxides of antimony were observed to have properties somewhat approaching to those of acids,

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[*] Annales de Chimie, tom. lxxxvi. p. 225. Nicholson's Journal, vol. xxxiv. p. 241.

[†] Annals of Philosophy, vol. iii. p. 248.

[‡] Annales de Chimie et Physique, tom. v. p. 162.

particularly in forming permanent and well marked combinations with alkaline bases. Berzelius has considered his third and fourth oxides, the white and the yellow, as acids; the former he names Antimonious or Stibious Acid, the other Antimonic or Stibic Acid: and their compounds he names Stibites and Stibiates. The first has little claim to this distinction; it is tasteless, insoluble in water, and the combinations it forms with alkalis have scarcely any saline characters. The second is insoluble in water, but its powder, even when carefully washed, reddens, according to Berzelius, the vegetable colours; its combinations, too, with the different bases seem to be more permanent. But still it may be doubted if it can be properly regarded as an acid. This property of reddening the vegetable colours, belongs to it also only when it is in the state of hydrate.

All the oxides of antimony are easily reduced by exposure to heat with carbonaceous matter.

Antimony suffers little change from water at a low temperature, but it decomposes it at that of ignition.

It is acted upon by a number of the acids. Its salts are distinguished by the orange-yellow precipitate thrown down from them by the alkaline hydro-sulphurets.

Sulphuric acid boiled on antimony oxidates it, sulphurous acid being disengaged, and a portion of the sulphuric acid being combined with the oxide, and forming a humid white mass. This is decomposed on the affusion of water, a sub-sulphate of antimony remaining undissolved, and a super-sulphate being dissolved; the solution becomes turbid without crystallizing when evaporated. Sulphurous acid, with the assistance of heat, oxidates the metal, and a compound is formed, which, according to Vauquelin, is a sulphuretted sulphite of antimony. The sulphurous acid may be combined with oxide of antimony, by adding it to the antimonial salts: it forms a white precipitate, sparingly soluble, and of an acrid taste, which is fused, and afterwards volatilized and decomposed by heat.

Nitric acid oxidates antimony, the degree of oxidation being so high when the acid is concentrated, that the oxide does not combine with so much of the acid as to form a proper solution; and scarcely even retains any acid in combination.

Muriatic acid acts very slowly on antimony, the disposing affinity it exerts not being sufficiently powerful to enable the metal to attract the oxygen of the water rapidly. A solution, however, is at length effected. The oxides of antimony are readily dissolved in it; and there are some indirect processes which the chemists were accustomed to employ to obtain the muriate. Thus, if metallic antimony be mixed with corrosive muriate of mercury in the proportion of six parts of the former to sixteen of the latter, or if sulphuret of antimony be used in the proportion of twelve parts to sixteen, on applying heat to either mixture in a retort, a muriate is obtained by distillation in a high state of concentration. Another process in the modern Pharmacopœias, is to mix brown oxide of antimony in powder with muriate of soda and sulphuric acid, and apply heat to the mixture in a retort; the muriatic acid, disengaged from the muriate of soda by the sulphuric acid, combines with a portion of the oxide of antimony, and the muriate is raised by sublimation. The product by either of these processes, is condensed, partly liquid, partly in the state of a soft mass, which, from its consistence, was named by the older chemists Butter of Antimony. When this is exposed to the air, it becomes liquid by attracting water; but if water be directly added, either to it or to the liquid solution, it decomposes it: a copious white precipitate is thrown down, formerly known by the name of Powder of Algaroth, which is the hydrated oxide, or rather a sub-muriate. The water above holds dissolved a super-muriate, having a great excess of muriatic acid. The muriate of antimony is highly caustic: it is very fusible, and volatile.

A similar compound is formed by the action of oxymuriatic or nitro-muriatic acid on antimony. Filings of antimony, projected into oxymuriatic gas, exhibit a very vivid combustion, and the concentrated muriate condenses on the sides and bottom of the vessel. Oxymuriatic acid gas transmitted through water over sulphuret of antimony, likewise oxidates and dissolves the metal. Nitro-muriatic acid is the solvent by which a concentrated and permanent solution is most easily obtained: it likewise dissolves the antimony in the native sulphuret, the sulphur being left undissolved: in both cases muriate of antimony is the product, if an excess of nitric acid is not employed; and by distillation it may be obtained pure. This affords the most economical process *. Considering this substance as a chloride, it consists, according to Dr J. Davy's analysis of it, of 60.42 of antimony, and 39.58 of chlorine.

The greater number of the other acids, though unable to oxidate and dissolve antimony, are capable of combining with its oxides, either directly by adding the oxide to the acid, or by a complex affinity, resulting from mixing, with a solution of an antimonial salt, the solution of a salt containing the acid with which the oxide is designed to be combined. Phosphate of antimony, obtained by such processes, has been described as being in the state of a soft mass, which is not crystallizable, and is changed by fusion into a transparent glass. Chenevix, in his researches on James's powder, found, however, that phosphoric acid could not, by any process of single or double affinity, be combined with oxide of antimony. The fluate, borate, and carbonate, are unknown.

Iodine acts on antimony nearly as it does on tin. It

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* Annales de Chimie et Physique, tom. iv. p. 165.

combines with it; and when water is added, it is decomposed, and hydriodic acid is formed, which, if too much water has not been added, retains the oxide of antimony dissolved.

The fixed alkalis combine with oxide of antimony in a high state of oxidation. This combination is best displayed in exposing antimony, or its native sulphuret, to heat with a large quantity of nitre; the former, for example, with six times its weight; the metal is completely oxidated, and this oxide remains in combination with the potash of the nitre. By washing with water, it is resolved into two compounds, one with an excess of alkali, which is dissolved; the other, which remains undissolved, and which consists of the oxide, with a smaller quantity of alkali so strongly combined with it, that it cannot be entirely removed by washing with water. This is what was formerly named Calcined or Diaphoretic Antimony. It was regarded as a pure oxide. Berthollet shewed that a part of the alkali of the nitre was contained in it: the quantity, according to Thenard, amounts to about one-fifth: and they appear to exist in very intimate combination. When washed with cold water, as long as the water extracts any alkali, it remains in the state of a powder, having an acrid and slightly metallic taste, very little soluble in cold water; but boiling water, if exposed to its action for some hours, dissolves a considerable portion of it. This solution contains the neutral compound; when evaporated to the consistence of syrup, it deposites a light granulated powder, and if farther evaporated, it affords a white semitransparent mass, which, when dried, appears like enamel. It is difficult to abstract the potash entirely from the oxide; it requires repeated digestion with nitric acid. From this analysis, Berzelius inferred, that it is composed of 20.8 of potash, and 79.2 of the peroxide, or, as he names it, Stibic Acid. A compound of this oxide, or acid, with ammonia, is, according to the same chemist, capable of being formed by digesting it in the state of hydrate with caustic ammonia; but it cannot be obtained neutral, as the heat necessary to expel the excess of ammonia, decomposes it. Stibiate of barytes, and stibiate of lime, as he names these compounds, are formed, he affirmed, on adding muriate of barytes, or of lime, to a solution of stibiate of potash; the first is insoluble in water, the second sparingly soluble; both are decomposed by nitric acid, which abstracts the acid and leaves the earth. By a similar process, analogous combinations may be formed with some of the metallic oxides *.

The less perfect oxide, or stibious acid, as Berzelius names it, is also capable, according to his experiments, of combining with alkaline bases: that of potash is formed by fusion of the oxide and alkali, with an excess of the former, lixiviating the product with cold water, then submitting the residual powder to the action of boiling water for two hours; a solution of the neutral compound is formed. And from this compounds with the earths and metallic oxides may be obtained, by adding to it solutions of their salts. But it is doubtful, as Gay Lussac has shewn, how far these products, and those of the stibic acid with metallic bases, are mixtures, or real combinations †.

Some ternary compounds of oxide of antimony with an alkali and acid, have been employed, from their medicinal powers. The most important of these is that obtained from the action of super-tartrate of potash on oxide of antimony. It is the tartrate of potash and antimony, long known by the name of Emetic Tartar, and superior to all the antimonials in the certainty of its operation. Various processes have been followed to prepare it, differing principally in the oxide that is employed. In the Edinburgh Pharmacopœia, the brown oxide of antimony, pre-

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* Nicholson's Journal, vol. xxxv. p. 38, &c.

† Annales de Chimie et Physique, tom. v. p. 162.

pared by deflagrating sulphuret of antimony with an equal weight of nitre, is ordered. Three parts of it in fine powder are boiled with four parts of super-tartrate of potash, and 32 parts of water, in a glass vessel. The liquor, after half an hour's ebullition, is strained through paper, and set aside to crystallize. Another process recommended by Bergman, is to employ the oxide prepared by decomposing muriate of antimony by carbonate of potash; two parts of this, washed with water and dried, being boiled with three parts of super-tartrate of potash in eighteen parts of water, and the liquor strained, and put aside to crystallize. This, with some modifications to render it more economical, has a place in the Dublin Pharmacopœia, the muriate to afford the oxide being prepared from sulphuret of antimony, by digestion with muriatic acid and a small portion of nitric acid. In the London Pharmacopœia, a similar oxide is obtained by digestion of sulphuret of antimony with nitre and sulphuric acid. In all these processes, the excess of tartaric acid in the super-tartrate dissolves a portion of the oxide of antimony, and part of the potash likewise enters into the combination, forming the tartrate of antimony and potash, which crystallizes. According to the analysis of this salt by Thenard, it consists of 38 of oxide of antimony, 16 of potash, 34 of tartaric acid, and 8 of water of crystallization *. Its crystals are triedral pyramids, which effloresce slightly on exposure to the air. It is soluble in about 15 parts of cold water, and in much less boiling water. In a state of solution it is slowly decomposed from the subversion of its acid: it is also decomposed by heat. Its value as an antimonial medicine is derived from the uniformity and comparative mildness of its operation.

Another important preparation, belonging to the same class, is that which has been named Phosphate of Anti-

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* Nicholson's Journal, 4to, vol. v. p. 271.

mony and Lime. An empirical remedy, known by the name of James's Powder, had been celebrated for its efficacy in the treatment of fever. Its composition was unknown, farther than that it was an antimonial preparation, until its analysis was undertaken by Dr Pearson *. He discovered that it consists of 43 parts of phosphate of lime, and 57 of oxide of antimony, part of this oxide (about 28 in 100 parts of the powder) being in a vitrified state, and insoluble in any acid. And he found, that by calcining equal parts of sulphuret of antimony and horn-shavings in an open fire, and afterwards exposing the powder in a covered crucible to a white heat for two hours, a preparation similar in chemical composition and medicinal operation is obtained †. In its formation the animal matter of the horn is decomposed by the heat, and its principles are dissipated, leaving the phosphate of lime, which is its base: the sulphur of the sulphuret is also expelled, and the antimony is oxidated, and the oxide is partially vitrified. It is uncertain, whether in either preparation the phosphoric acid remains exclusively united with the lime, and this phosphate of lime is merely mechanically mixed with the oxide of antimony; or whether it is in combination both with the lime and the oxide, forming a ternary compound.

Antimony combines with sulphur by fusion, and forms a compound similar to the native sulphuret. In this combination, according to Bergman, and also to Proust, 100 parts of antimony are combined with 35 parts of sulphur by weight ‡: Vauquelin gave the proportions of 100 with 33.33; and Dr Thomson has from analytic experiments inferred, those of 100 with 35.55 ||; Berzelius those of 100 with 37.25.

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* Philosophical Transactions, 1791, p. 317.

† In the London Pharmacopœia, the proportions have been altered to one of the sulphuret of antimony to two of horn.

‡ Journal de Physique, tom. lv. p. 352.

|| Annals of Philosophy, vol. iv. p. 95.

The oxides of antimony appear also to combine with sulphur. According to Proust, indeed, when sulphur is heated with oxide of antimony, either at the minimum or maximum of oxidation, the oxide is always decomposed, sulphurous acid is disengaged, and a metallic sulphuret formed; and if oxide of antimony appear in certain preparations to be combined with sulphur, it is only, he supposes, by the medium of metallic antimony. This is, however, only an hypothetical assumption: the disengagement of sulphurous acid does not prove that a complete de-oxidation takes place; and there are facts to be immediately stated, which prove, that sulphur and the oxides of antimony combine.

From the sulphuret of antimony being procured native, and from the metal having been even for a long time scarcely known, it has happened that many preparations have been formed from the sulphuret, instead of from the pure metal, and have derived from this some peculiarities of composition. Of some of these, which are still frequently objects of attention to the chemist, as well as to the physician, it is necessary to take notice.

If the sulphuret be exposed in a shallow earthen vessel to a heat not sufficient to fuse it, sulphureous fumes arise; and if the fire be gradually raised, it is converted into a grey powder, which is an imperfect oxide, retaining a portion of sulphur. If this be exposed in a crucible to an intense heat, it melts, and forms a glass of a reddish brown colour. This is what was known by the name of *Glass of Antimony:* it may be named the Vitrified Sulphuretted Brown Oxide. It generally contains, as Vauquelin discovered, a portion of silex, amounting to 9 or 10 parts in 100, derived from its action on the crucible in which it is fused *. Proust has considered it as a compound of oxide of antimony and sulphuret of antimony, in the proportion

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* Annales de Chimie, tom. xxxiv. p. 138.

of about eight parts of oxide, and one of sulphuret, and has shewn that it is formed by melting the oxide and sulphuret of antimony in these proportions. But it is more probable, that, in such an experiment, the metal of the sulphuret shares the oxygen of the oxide, and that the compound is a sulphuretted oxide. According to Thenard, it is the brown oxide, or that containing 0.16 of oxygen, that is its basis.

If equal parts of sulphuret of antimony and nitre in powder, are projected into an ignited crucible, a vivid deflagration takes place: the greater part of the sulphur is converted into sulphurous acid, and dissipated; and the antimony is oxidated, while the oxide retains a portion of sulphur combined with it. This preparation has been known by the name of *Saffron of Antimony*. The principal difference between it and the preceding one is, that the proportion of sulphur is larger, and perhaps the metal is less perfectly oxidated. Proust considers it as oxide of antimony and sulphuret of antimony, in the proportions of eight of the former and two of the latter; and it is not impossible but that, from the rapidity of the deflagration, a portion of the metal may escape oxidation.

With a larger proportion of nitre the preparation already noticed is obtained, named Calcined or Diaphoretic Antimony. Three parts of nitre, with one of the sulphuret, are deflagrated, and the residual matter is exposed in the crucible to heat, until it become white. It is then washed with water and dried. From the large quantity of nitre employed, the antimony is fully oxidated, and the oxide remains combined with a portion of potash. This compound has been already considered.

When sulphuret of antimony is fused with potash, and thrown into water, or when an alkaline solution is boiled upon it, (six parts of sub-carbonate of potash, one-twentieth of the weight of this of sulphuret of antimony, and 20 parts of water being boiled together), the antimony is oxidated, and combined with the sulphur and sulphuretted hydrogen existing in the solution, so as to be soluble in water. The liquor, if strained while hot, is transparent and nearly colourless; but as it cools, it deposites a powder of a lively brick-red colour, known to the chemists by the name of *Kermes Mineral*, and much used on the Continent as an antimonial medicine. If, instead of allowing the liquor to cool, diluted sulphuric acid is added to it, a little sulphuretted hydrogen is disengaged, and a copious orange-coloured precipitate is thrown down, which has been known by the name of *Golden Sulphur of Antimony*, and has been more used in this country than the kermes, though now little employed. It has been an object of much investigation to determine the nature of these preparations, and the chemical distinctions between them. Bergman discovered the existence of sulphuretted hydrogen in them, and Thenard has analysed them minutely. He found, that the kermes mineral consists of 72.760 of the brown oxide of antimony, 20.298 of sulphuretted hydrogen, and 4.156 of sulphur; while the other, the golden sulphur, as it is named, is composed of 68.3 of the orange oxide of antimony, with 17.877 of sulphuretted hydrogen, and 11 or 12 of sulphur *. The principal difference between these preparations, he regards as depending on the degree of oxidation of the base, which in the golden sulphur is rather higher than the other. But as the two preparations may be obtained from the same solution, there appears to be no cause by which a difference of oxidation can be produced: the base must be the same; and the opinion of Trommsdorff † is more probable, that the essential difference between them is in the golden sulphur containing a larger proportion of sulphur. This follows from their mode of preparation. The kermes is merely depo-

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* Annales de Chimie, tom. xxxii. p. 268.

† Ibid. tom. xxxiv. p. 152.

sited from the solution, and the portion of sulphur and sulphuretted hydrogen combined with the oxide, must be only the portions which it can attract, while quantities of each of them must still be retained by the alkali. The golden sulphur is precipitated by the addition of an acid, which must saturate the alkali: the sulphuretted hydrogen combined with that alkali appears to be disengaged, while the sulphur combined with it must be precipitated: and hence more sulphur must enter into the composition of the precipitate, than into the composition of the other, which is deposited without this saturation of the alkali by an acid. The proportion of sulphur in the former will even be different, if the acid is gradually added, in the quantity that first falls down, from what is in the quantity last precipitated.

Sulphuretted hydrogen added to antimonial salts, gives an orange-coloured precipitate from combining with their oxide; and a similar precipitate is formed by the hydrosulphurets and sulphuretted hydro-sulphurets.

Antimony combines with phosphorus by the usual methods of forming the metallic phosphurets. The phosphuret of antimony presents brilliant facets, is of a white colour, brittle, and fusible.

Antimony combines with the greater number of the metals: in general, its alloys are brittle, and of a foliated texture. Few of them have been applied to any use. It very much impairs the ductility of gold, even when in a quantity less than $\frac{1}{1000}$ of the mass. The largest quantity of antimony which gold can fix, appears to be about 1 part to 15. The alloy is of a dull grey colour, brittle, and of a fine grain. Silver is rendered brittle by it, as is platina; nor is the antimony easily expelled entirely from either metal by heat. It does not easily amalgamate with quicksilver, and the amalgam obtained by heat is very imperfect. Copper forms with antimony a pale and brittle alloy: when the proportions are equal parts of the two metals, it is of a violet colour, and has a striated texture. Iron and antimony unite by fusion: the alloy, when of equal parts, is hard, brittle, and in its fracture presents small facets: the magnetic quality of the iron is entirely destroyed. The alloy of antimony with lead, is almost the only one applied to any use: it forms the the metal of which printing-types are cast. The proportions are various, but, in general, it consists of 80 parts of lead, with from 15 to 25 of antimony, the proportion of antimony being larger as the type is to be small. It is tolerably hard; has considerable tenacity; and it perhaps derives from antimony the property of expanding in becoming solid, whence it takes a fine impression from a mould, and is therefore well adapted to the purpose to which it is applied. Antimony, combined with tin, adds to its hardness, but renders it more brittle. According to Thenard, however, this is owing to the presence of lead. Four parts of tin, and one of antimony, form an alloy which is very ductile; and even when composed of equal parts, considerable ductility remains. It was observed by Thenard, that the two metals exert such an action on each other, that the usual effects from re-agents on them are not obtained *; both, for example, being precipitated from the solution of the alloy in muriatic acid by the affusion of water, though tin alone is not precipitated. According to the experiments of Chaudet, the presence of antimony counteracts the solution of tin in muriatic acid, and this in proportion to its quantity; and if the proportion of tin be large, it is dissolved without any of the antimony passing into solution †. Zinc forms with antimony a hard and brittle alloy. Its alloys with nickel, cobalt, and manganese, have scarcely been examined. It forms with arsenic

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* Philosophical Magazine, vol. xxiv. p. 256.

† Annales de Chimie et Physique, tom. iii. p. 376.

a hard and brittle alloy, which is easily melted: its alloys with bismuth are also brittle.

Oxide of antimony appears to combine with some other metallic oxides. A combination of it with oxide of lead forms the paint known by the name of Naples Yellow. Different recipes, varying much in the proportions of the ingredients, have been given by Beckman *.

Oxide of antimony combines with, and promotes the vitrification of some of the earths, giving to their glass a hyacinthine colour.

Antimony is principally used in the formation of certain alloys, especially that for forming printing-types: its oxides are used in the composition of pastes and enamels; and it is extensively employed in various combinations in the practice of medicine.

CHAP. XVI.

ARSENIC.

The term Arsenic appears to have been applied by the ancients to the native combinations of the metal which has now received that name, with sulphur. Avicenna mentions white arsenic; and this substance, sublimed in the roasting certain metallic ores, was known to the alchemists. Lemery and Schroder first described processes by which metallic arsenic may be obtained from it. Brandt examined the properties of this metal, and the investigation was prosecuted by Macquer, Bergman, and Scheele.

Arsenic occurs native, alloyed with iron and small por-

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* Philosophical Magazine, vol. iii. p. 278.

tions of other metals, and mineralized by oxygen, and by sulphur, and in the state of acid combined with lime. Its most common ores are the sulphurets, the yellow being named Orpiment, the red Realgar.

As metallic arsenic is applied to no use, it is not extracted from its ores, but is obtained in the state of the white oxide. The greater part of this is procured in roasting other metallic ores, particularly those of cobalt, in which arsenic is contained. The roasting is performed in furnaces with flues, in which the vapours of oxidated arsenic are condensed, and the oxide is purified by sublimation. Sometimes it is obtained by sublimation from arsenical pyrites. It is this white oxide that is known in common language by the name of Arsenic. The process is carried on in Saxony and Bohemia on a large scale *.

To obtain the arsenic in its metallic state, the common process is to mix the white oxide with an equal weight of black flux, and expose the mixture to heat in a glass tube or retort; or if a larger quantity be operated on, in a crucible, to which another is luted so as to be close. On raising the heat to ignition, the oxide is reduced, and the metal sublimed, and, when the apparatus is cold, it is obtained in the form of a brilliant crust, which has a crystalline form, and to which there frequently adhere regular crystals, prismatic or octaedral.

Arsenic in its metallic state is of a bluish grey colour, with considerable lustre, liable to tarnish and become black from exposure to the air. Its texture is broad striated: it is not very hard, and is extremely brittle, so as to fall into fragments from a slight blow. Its specific gravity is stated by Bergman at 8.310; by Brissón at 5.763. In its solid state, it is inodorous; but when volatilized, its vapour has a strong peculiar smell, resembling the smell of garlic. Its oxide is the most violent of all the mineral poisons.

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* Journal de Physique, tom. li. p. 44.

Arsenic is so volatile that its fusing point can scarcely be ascertained: it passes into vapour when heated, without becoming previously fluid. Its vaporific point is, according to Bergman, about 388 of Fahrenheit*.

This metal is very susceptible of oxidation; it suffers it even from exposure to the atmospheric air, becoming black, and falling into powder. When heated, the oxidation proceeds rapidly: at a temperature about that at which it is volatilized, it forms a white smoke, consisting of the oxide in vapour, and distinguished by the peculiar garlic smell. When the heat is raised a little higher, the arsenic burns with a dull blue flame.

The white oxide of arsenic is possessed of peculiar properties. Instead of being insipid, as the greater number of metallic oxides are, it has an acrid taste, and is corrosive; it is soluble in water, and its solution in boiling water deposites, on cooling, crystals in the form of tetraedral prisms, or octaedrons. It has been said to redden the infusion of litmus, and it combines with the alkalis. From these properties, Fourcroy has proposed to consider it rather as an acid than an oxide, and named it the Arsenious Acid, an arrangement for which there is some foundation. Yet, as Berthollet has remarked, it is on the whole more analogous to the highly oxidated oxides; it does not exert a greater action on the alkalis than they do; and to this it may be added, that it combines with the acids, and forms saline compounds. I have not been able to observe that it has even any effect on the colour of litmus. This oxide is volatile, but less so than the metal: it requires, according to Bergman, a temperature of about 415° of Fahrenheit to pass into vapour. If heated in close vessels it may be fused. By sublimation it may be obtained in the form of a dense solid cake. Its specific gravity is 5.000; that of the unsublimed oxide is 3.706. Its solubility in water

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* Chemical Essays, vol. ii. p. 282.

has been variously stated. According to Bergman, it requires only 80 parts of water at 60° for solution, and 15 parts at 212° : while, according to other statements, 80 parts of boiling water are necessary to dissolve one part. Klaproth submitted this to more minute examination. He found, that 1000 parts of cold water are necessary to dissolve $2\frac{1}{2}$ of the oxide. 1000 of boiling water dissolve $77\frac{3}{4}$; it is only in this way that water can be saturated with it; and when cold it still retains 30 parts, or 3 in 100 parts. According to Fischer, white oxide of arsenic is insoluble in water, and its apparent solution takes place only from a change of composition, the dissolved portion becoming acid, by acquiring oxygen from the portion which remains undissolved. Mr Phillips has shewn, that these statements are inaccurate, and that the dissolved and undissolved portions are perfectly the same. As so much more of the oxide remains dissolved after the action of boiling water, than what cold water can directly dissolve, it might be supposed that it passes to the state of a hydrate. Klaproth found, however, that a certain portion being dissolved, gained no weight when recovered in a crystalline form by evaporation, and contained therefore no water *.

Arsenic is capable of passing to a higher degree of oxidation, whence it acquires the properties of an acid. This was discovered by Scheele. This acid may be obtained by distilling nitric acid from the white oxide, but the process is slow and imperfect. It succeeds better when the oxide is previously dissolved in muriatic acid. On this is founded the process of Scheele. Two parts of the white oxide are dissolved in seven parts of muriatic acid, with the assistance of heat, and there are added to this solution, in a retort, three parts and a half of nitric acid : the nitric acid affords oxygen to the oxide; and much nitric oxide gas is disengaged. The distillation is continued until this

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* Annals of Philosophy, vol. iv. p. 133. vii. p. 33. viii. p. 152.

ceases: one part of oxide of arsenic is again added, and a moderate heat applied until it is dissolved. One part and a half of nitric acid is lastly poured on the solution, and the whole is distilled to dryness, the fire being raised towards the end of the distillation, so as to bring the bottom of the retort to a red heat. The solid Arsénic Acid is thus obtained *.

The acid powers of this substance are very distinct. It is abundantly soluble in water, requiring only six parts for its solution at 60°, and not more than two parts at 212°: its taste is sour: it reddens the vegetable colours, neutralizes the alkaline properties, and combines with the metallic oxides and earths. Its solution, when concentrated, is of an oily consistence, and by evaporation affords small irregular crystals. When the water is evaporated, it forms a solid mass of a white colour, which, by raising the heat to ignition, is melted, and forms a translucent glass. It is not volatile,—a proof of the great condensation in the combination, since not only is the compound inferior in volatility to the mean volatility of its constituent principles, but is even less volatile than the one which is of greatest fixity.

By a strong heat this acid is decomposed, part of its oxygen is expelled, and it is reduced to the white oxide. It is also decomposed by inflammable bodies, which abstract its oxygen. The transmission of a current of hydrogen gas through its concentrated solution, appears sufficient from the experiments of Pelletier, to reduce it to the metallic state†. Sulphur and charcoal at a high temperature decompose it, as do a number of the metals.

The white oxide and the acid appear to be the only compounds arsenic forms with oxygen. Different proportions have been assigned to both of them.

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* Chemical Essays, p. 143.

† Memoires de Chimie, tom. i. p. 21.

Prouts, who first investigated the subject with precision, inferred, that the oxide is composed of 75.2 of metal, and 24.8 of oxygen, or 100 with 33. Rose and Bucholz obtained from their experiments almost the same result. Those of Thenard assign the proportion of 100 with 34.7; and those of Berzelius give almost precisely the same,—100 with 34.26. According to Proust, the acid is composed of 100 of arsenic, with 52.9 of oxygen; and with this estimate also the experiments of Rose and Bucholz coincide. Thenard gave the proportion of 100 with 56.25; and Berzelius that of 100 with 51.43. These results do not differ greatly from each other. In some subsequent experiments, other proportions were stated by Berzelius; the oxide being inferred to be composed of 100 of metal with 47.6 of oxygen, and the acid of 100 with 71.4. Dr Thomson, however, repeating the experiment of the conversion of arsenic into arsénic acid by the agency of nitrous acid, obtained as the result, from the increase of weight, 100 of the metal with 52.4 of oxygen. And, as he justly remarks, there is no apparent source of fallacy in the experiment, and certainly none that can account for such a difference as that stated in the experiments of Berzelius. Coinciding nearly with the others also, it must probably be correct. If the proportion of oxygen in the oxide be to that of the acid as 2 to 3, as is probable, both from analogy, and from their nigh approximation to this in the experimental results, then, admitting the acid to be composed of 100 of arsenic and 52.4 of oxygen, the oxide will consist of 100 with 34.93 *. Berzelius has since admitted the inaccuracy of his former statements, and has given as the proportions,—in the oxide 100 of arsenic with 31.77 of oxygen, in the acid 100 with 52.96, which is in the ratio of 3 to 5 †.

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* Annals of Philosophy, vol. iii. p. 93. iv. p. 171.

† Annales de Chimie et Physique, tom. v. p. 179.

Both the oxide and the acid of arsenic are capable of forming a number of combinations with the other chemical agents. Those of the oxide may first be considered.

It unites with the different acids, though it is difficult to obtain these compounds neutral. The same combinations are in general produced by the action of the acids on metallic arsenic: the acid first causing the oxidation of the metal, and then combining with the oxide.

Sulphuric acid does not act on arsenic in the cold, but, boiled on it, the metal is oxidated, and this oxide combines with a part of the acid. The acid, when boiled on the oxide, dissolves a portion of it, and deposites, as it cools, crystalline grains less soluble than the oxide, and which are decomposed by heat *.

Nitric acid speedily oxidates metallic arsenic. When diluted, it dissolves the oxide: the compound being sparingly soluble, is deposited on evaporation. The concentrated acid, in acting on the oxide, communicates more oxygen to it; and, when distilled from it, converts it, though imperfectly, into arsénic acid.

Muriatic acid exerts a very weak action on metallic arsenic, unless it be boiled on it. The metal is then oxidated from decomposition of the water, and hydrogen gas is disengaged, having a very fœtid odour, which it owes to a portion of arsenic that it holds in solution. The acid dissolves by boiling one-third of its weight of the white oxide; the muriate of arsenic being in a great measure deposited when the solution cools. This salt is sparingly soluble in boiling water: it may be obtained crystallized: it is volatile, being in a close vessel completely sublimed †. The chemists were also accustomed to obtain muriate of arsenic in a concentrated state, by exposing a mixture of corrosive muriate of mercury and metallic arsenic, in the

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* Bergman's Essays, vol. ii. p. 96.

† Ibid. p. 296.

proportion of about six of the former to one of the latter, to heat in a retort; the acid, with a portion of the oxygen, being transferred to the arsenic, and the muriate distilling over, and being condensed, partly in the state of a dense liquid, and partly in a congealed state; the latter was formerly named Butter of Arsenic. Though it appears probable, that in this combination the metal may be in a higher state of oxidation than in the solution obtained by boiling the oxide in muriatic acid, they scarcely differ, according to Bergman, but in concentration. It emits white acrid vapours: absorbs water from the atmosphere, but is decomposed by the affusion of water: by the action of alkalis, a precipitate is thrown down from it. By spontaneous evaporation, it deposites pellucid crystals, which are sparingly soluble in water.

Oxymuriatic acid acts with energy on metallic arsenic. When fragments of it are projected into the gas, they are inflamed, and the concentrated muriate is formed. Considering this as a chloride, it consists, according to Dr J. Davy's analysis of it, of 39.52 of arsenic, and 60.48 of chlorine. The liquid oxymuriatic acid, digested on the white oxide, converts it into arsénic acid.

The other acids scarcely act on arsenic. Fluoric acid dissolves the oxide, and forms crystalline grains, as does also phosphoric acid. Boracic acid dissolves the oxide: the compound is soluble in water, and the solution, on evaporation, deposites it partly in powder, partly in slender crystals. Carbonic acid does not dissolve the oxide, at least water impregnated with it does not dissolve more than pure water would do *.

Oxide of arsenic is capable of combining with the alkalis. They unite by fusion. Potash, at the temperature of ignition, unites with twice its weight of the oxide, the volatility of which it completely restrains. Soda can fix

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* Bergman's Essays, vol. ii. p. 295, 298.

three times its weight. The solutions of these alkalis boiled on the oxide, also dissolve a considerable proportion of it: the solution, when concentrated, becomes thick and tenacious, of a brown colour, and emits a disagreeable odour. The oxide is partly, though not entirely, precipitated by acids. Ammonia dissolves a portion of the oxide, as does lime-water; and lime, and some of the other earths, combine with it by fusion *.

In these chemical relations, the oxide of arsenic appears nearly equally energetic in its action on acids and on alkalis. When more highly oxidated, the acid powers predominate; and this acid, the Arsénic, combines with the alkalis, the earths, and the metallic oxides, and forms neutral combinations, denominated Arseniates.

The Arseniate of Potash was discovered by Macquer, prior even to the discovery of the arsénic acid by Scheele. It was obtained by an indirect process. Equal parts of white oxide of arsenic and of nitre were exposed to heat in a retort; the heat being continued until the copious red vapours, which are at first produced, have ceased. On adding to the residual matter hot water, it is dissolved, and, by evaporation, affords large regular crystals, the form of which is a tetraedral prism acuminated by four planes. The theory of the process is evident; the nitric acid of the nitre is decomposed: its oxygen transferred to the oxide of arsenic converts it into arsénic acid, which combines with the potash of the nitre. The product has always an excess of acid: it is fused by heat, but is not decomposed. The neutral salt, formed by the direct combination of the acid and alkali, does not crystallize with so much regularity, and is deliquescent.

Arseniate of soda is formed by the same indirect process as arseniate of potash, substituting nitrate of soda for nitre. It crystallizes in hexaedral prisms.

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* Bergman's Essays, vol. ii. p. 295.

The Arseniate of ammonia can be formed, according to Bergman, by exposing to heat a mixture of nitrate of ammonia, and of oxide of arsenic; but as the ammonia is liable to be decomposed, it is better prepared by the direct combination of its constituent principles. It crystallizes in rhomboidal prisms. It is decomposed by heat; the ammonia being at first expelled, and, towards the end of the process, decomposed.

Arsénic acid forms combinations with some of the earths. When arseniate of soda is dropt into muriate of barytes, crystalline scales are deposited after some time, which are insoluble in water. This compound consists, according to Berzelius, of 42.97 of arsénic acid, and 57.03 of barytes. The compound with lime is sparingly soluble, but is rendered more soluble by an excess of acid; and, in this state, crystals are obtained by evaporation of the solution. The salt formed with magnesia, is also of sparing solubility when neutral, but, with an excess of acid, becomes soluble, and forms a gelatinous mass by evaporation. The arseniate of alumina is nearly insoluble. These salts are not decomposed by heat alone, but, if a small portion of charcoal be added, the acid is decomposed, and oxide of arsenic is sublimed *.

Arsénic acid acts on several of the metals, and is capable of combining with the greater number of them when oxidated. These combinations have not been much examined. We are principally indebted to Scheele for our knowledge of them.

On gold arsénic acid exerts no action, neither does it occasion any precipitate in the solution of gold. Silver is not acted on by the acid, but the alkaline arseniates decompose nitrate of silver, and the arsénic acid combines with the oxide of silver: the compound is, to a certain extent, soluble in water, and is decomposed by heat, oxide

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* Scheele's Essays, p. 165.

of arsenic being sublimed. On quicksilver, arsénic acid exerts no action in the humid way, but, when exposed to a high temperature, the acid is in part decomposed, the mercury is oxidated, and this, combined with the remaining acid, forms an arseniate of mercury, which, by a farther application of the heat, suffers decomposition. Digested with copper, arsénic acid forms a green solution, and a powder of a bluish-white colour is precipitated, which is arseniate of copper. By heat it fuses into a glass. This combination exists native, forming a copper ore. Iron is dissolved by arsénic acid, aided by a moderate heat: the solution, by evaporation, becomes gelatinous. Arseniate of iron is, as well as arseniate of copper, a native production. Lead becomes black when arsénic acid is digested on it; and, when they are exposed together to heat, the acid is in part decomposed, oxide of arsenic is sublimed, and arseniate of lead remains, which may be fused into a white glass. The arsénic acid precipitates oxide of lead from the greater number of its saline combinations, by combining with it, and forming an insoluble compound; and a similar compound is formed, by mixing any of the salts of lead with any of the soluble arseniates,—a property which affords the best mode of separating arsenic from other metals. Arseniate of lead, according to Thenard's analysis of it, is composed of 35.5 of arsénic acid, and 64.5 of oxide of lead; according to Berzelius of 34 and 66. Arsénic acid, by digesting on tin, oxidates and dissolves a portion of it, forming a gelatinous solution, and it produces a precipitate from some of the salts of tin. Zinc is dissolved by it, with effervescence from the disengagement of hydrogen, and a black powder separates, which is arseniate of zinc. When zinc filings and arsénic acid are heated together, an inflammation and detonation take place, and arsenic and oxide of zinc are volatilized. The solutions of zinc are decomposed by the arseniates. Nickel is dissolved by arsénic acid: the solution has a green colour, and a green powder is precipitated: the acid does not precipitate oxide of nickel from its solutions, but the arseniates produce a precipitate when added to the salts of nickel. The acid, when digested on cobalt, acquires a rose colour; and a precipitate of a similar colour is formed by adding any of the alkaline arseniates to a solution of cobalt. Manganese is dissolved in small quantity by it; and, if heated with the acid in its concrete state, converts it into oxide of arsenic. Bismuth, by digestion with the liquid acid, is converted into a white powder, and its oxide is precipitated by it from its solution in other acids. Antimony likewise forms a white powder, by digestion with arsénic acid; and, if distilled to dryness, an inflammation takes place as soon as the mass passes into fusion. By arsenic itself, arsénic acid is converted into the white oxide [*].

Arsenic is dissolved by hydrogen. Scheele proved, that the hydrogen gas which is disengaged when zinc is acted on by arsénic acid, holds arsenic dissolved; as, when detonated, it deposited a film of the metal. Proust shewed that it can be procured with more facility, by mixing diluted sulphuric acid, zinc, and oxide of arsenic; the hydrogen disengaged reducing the oxide, and dissolving the arsenic [†]. Its properties were afterwards examined by Trommsdorff. It has the peculiar arsenical odour; is not absorbed by water; does not alter the colour of litmus; is heavier than pure hydrogen, or than sulphuretted hydrogen; its specific gravity, compared with atmospheric air, being 0.5293. It is decomposed with detonation when kindled with atmospheric air or oxygen: when kindled with the former, it burns with a blue flame, deposites the greater part of the arsenic it holds dissolved, in the metallic state: when detonated with the latter, the temperature being higher, the arsenic, as well as the hydrogen,

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[*] Scheele's Chemical Essays, p. 168.

[†] Journal de Physique, tom. li. p. 175.

combines with oxygen, and it passes to the state of the white oxide. It is also decomposed by nitric oxide gas, and oxymuriatic acid gas. The latter acts on it in the cold: when slowly introduced to it, the arseniated hydrogen gas is diminished in volume, and metallic arsenic is deposited, which, if the addition of the oxymuriatic acid gas be continued, is changed into oxide of arsenic. When nitrous acid is poured into a phial containing it, the gas is kindled with detonation. Sulphuric acid precipitates a metallic film from it; and nitro-muriatic acid first precipitates, and then oxidates the metal. It decomposes, and is decomposed, by a number of metallic solutions. It does not combine with the alkalis *.

Stroymeyer added some facts on arseniated hydrogen. He found it to be most easily produced by digesting an alloy of 15 parts of tin, and 1 of arsenic, with muriatic acid. The gas disengaged has a very fœtid smell, and proves peculiarly fatal to animal life. Though aeriform, it was condensed in part into a liquid, by immersing it into a mixture of snow and muriate of lime †. Gehlen, the German chemist, who fell a victim to the deleterious agency of this gas, to which he had exposed himself while making experiments upon it, employed a different process for its production,—that of heating arsenic with a solution of potash. When the liquor becomes concentrated, hydrogen gas is disengaged, which continues until the mass becomes dry, and of a deep reddish brown colour. On adding water to this mass, it dissolves, becomes heated, a rapid ebullition takes place, and arseniated hydrogen gas is disengaged, probably more pure than that by the other processes. Gay Lussac has supposed, that the red coloured matter is a mixture of arseniate and arseniuret of potash. This arseniuret, or compound of metallic arsenic and pot-

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* Nicholson's Journal, vol. vi. p. 200.

† Ibid. vol. xix. p. 381.

ash, decomposes water rapidly, and the nascent hydrogen combines with a portion of the arsenic, so as to form the arseniated hydrogen *.

It is not certain if this compound has been obtained pure; it varies much in specific gravity; and hydrogen gas is probably evolved alongst with it in the processes by which it is obtained. There is little certainty, therefore, with regard to any estimate of its composition. According to Trommsdorff, a cubic inch of it weighs 0.2435 grain; a cubic inch of pure hydrogen weighs 0.0353; he inferred from this, that this gas must be composed of .0353 hydrogen, and .2082 of arsenic by weight. Stroymeyer, from the results of its decomposition by nitric acid, concluded that it consists of 0.219 of hydrogen, and 10.600 of arsenic. Davy found, that when it is decomposed by electricity, there is no change of volume, but the arsenic is thrown down in a brown powder, not perfectly metallic. When decomposed by potassium, the volume is enlarged; and Gay Lussac found, that in its decomposition by tin heated in it, there is an expansion of 100 volumes into 140.

There is reason to believe that arsenic combines with hydrogen, so as to form a solid compound. When it is employed in the decomposition of water by galvanism, forming the negative wire, it becomes dark-coloured, and a brown powder is thrown down: and it has appeared to me in making this experiment, that although there is an evolution of hydrogen at the wire, it is less than when a platina wire is employed. The brown powder is probably a hydruret of arsenic, containing less hydrogen than the gaseous compound.

Arsenic does not combine with carbon by any direct process; but there is a singular product,—the Fuming Liquor of Cadet, as it has been named,—which, according to Davy, contains arsenic and charcoal, probably with

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* Annales de Chimie et Physique, tom. iii. p. 135.

hydrogen *. It is obtained by distilling oxide of arsenic with an equal weight of acetate of potash. The product is a liquor of a red colour, having a very fœtid smell, and which emits copious fumes. The Dijon academicians found, that when poured out so as to be freely exposed to the air, it emitted a very thick smoke, and burst into a rose-coloured flame. In the formation of this product by the process of Cadet, gases are disengaged having an intensely fœtid smell, inflammable, and which contain charcoal, arsenic, and hydrogen.

Arsenic combines with sulphur by fusion, or by sublimation, and similar combinations are established when the oxide, or even the acid, is heated with sulphur; a portion of the sulphur attracting the oxygen of the oxide or acid, and forming sulphurous acid gas, which Bergman observed to be always disengaged. The compounds are of a red or a yellow colour, according to the proportions or the mode in which they are formed, the yellow being produced when the arsenic and sulphur are united without fusion, the red when the combination is accompanied with fusion. They resemble the native arsenical ores, Orpiment and Realgar, and have hence received the same names. The yellow is of a plated or flaky texture, the red may be obtained crystallized. Different opinions have been maintained with regard to their composition. In the native compounds, the arsenic had been supposed to be oxidated in the combination. Proust and Thenard shewed that it is in the metallic form; and the latter chemist maintained the opinion which had also been held, that the difference in the two compounds depends on the proportions of their elements, the red being composed, according to his analysis, of 75 of arsenic, and 25 of sulphur; the yellow of 57 and 43 †. Laugier submitted them anew to

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* Philosophical Transactions, 1810.

† Journal de Physique, tom. lxiv. p. 25.

analysis to determine this, Hauy having suspected their identity, from finding the primitive form of their crystals to be the same. He found that any mixture of arsenic and sulphur, exposed in a close vessel to a heat sufficient to produce fusion and sublimation, is converted into a matter of an orange yellow or red colour, having the transparency of glass, which is a sulphuret, composed always of the same proportions,—58 of arsenic, and 42 of sulphur. The native orpiment and realgar contain less sulphur,—the yellow containing about 38 in 100 parts, the red 30 or 31. This excess of arsenic in both he considers not essential to the composition, but adventitious; hence the identity of their crystalline forms; it is expelled by heat, and the proportions of the artificial sulphuret are established [*].

These compounds are decomposed by the fixed alkalis with the aid of heat; but in the humid way the alkalis render them soluble in water; from this solution a precipitate is thrown down of a lively yellow colour by an acid. Hence a similar combination may be formed by boiling a solution of potash with arsenic and sulphur: and the yellow precipitate is also formed by the action of sulphuretted hydrogen on any arsenical solution. Lime boiled in water with a portion of orpiment, forms a liquor which has been used to cause the hair to fall off when it is applied to a part, and also as a test-liquor to discover the presence of lead in wine.

Arsenic combines with phosphorus, by exposing equal parts of them to a moderate heat in a retort. The compound is a shining mass of a black colour, which decomposes by exposure to the air, and burns when projected on burning fuel. A similar combination is obtained by heating phosphorus with oxide of arsenic.

Arsenic combines with the greater number of the metals,

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[*] Annales de Chimie, tom. lxxxv. p. 59.

these combinations being formed by exposing to heat a mixture of the white oxide, and of the black flux, with the metal with which the arsenic is designed to be combined. It in general impairs greatly the ductility of those metals which are ductile, and renders fusible those which are refractory in the fire: it often also communicates greater hardness and brilliancy: it destroys the magnetism of the metals possessed of this property.

Gold has its ductility impaired by a very small quantity of arsenic, not exceeding, according to Hatchet's experiments, $\frac{1}{900}$ of the gold; and when the quantity is greater, the alloy is quite brittle, and very fusible: it is of a grey colour, and the arsenic is not easily separated from it. With silver arsenic unites, especially when a little alkali is added, which prevents the volatilization of the arsenic: the alloy is very brittle, and the arsenic can scarcely be altogether expelled from it. Platina it renders more fusible; and hence, as has been already stated, it is employed in one of the processes by which that metal is worked, the arsenic being afterwards volatilized from the platina by exposure to a sufficient heat. It does not easily amalgamate with quicksilver, but, by continued trituration, aided by a moderate heat, the combination may be effected. The amalgam is of a grey colour. With copper it can combine without difficulty, either by fusing them together in a covered vessel, or by exposing to heat copper granulated, or in thin plates, with oxide of arsenic and charcoal powder. The alloy is flexible and malleable, of a white colour, and is susceptible of a high polish, but it tarnishes and becomes black on exposure to the air: it is sometimes used instead of pure copper in plating with silver. Iron is rendered brittle and of a white colour by an alloy of arsenic. Lead combines with about one-sixth of its weight of it, and becomes brittle and of a dark colour. Tin, in combining with arsenic, acquires a very white colour, becomes harder, and more brittle. Zinc unites with it by being exposed to heat with oxide of arsenic, but the properties of the alloy have not been examined. Nickel exerts a strong attraction to it, as, when they are united, the arsenic is not easily separated: the compound is hard and brittle. It has also a strong affinity to cobalt, as, when naturally combined, which they frequently are, they are separated with difficulty.

Arsenic precipitates several of the metals from their solutions, particularly gold, silver, platina, and quicksilver. Its oxide combines also with some of the other metallic oxides. A combination of this kind with oxide of copper, forms a pigment of a fine green colour, discovered by Scheele, known by the name of Vegetable Green. To prepare it, two pounds of sulphate of copper are dissolved in twelve pounds of water, in a copper vessel, placed over the fire. Two pounds of the potashes of commerce, and eleven ounces of white oxide of arsenic in powder, are dissolved in another vessel, in four pounds of water. This solution, strained through linen, is added by small quantities at a time to the former solution, stirring it constantly. A precipitate is deposited of a green colour, which, after being washed with warm water, is to be dried with a moderate heat. It consists of oxides of copper and arsenic, the former being separated by the potash from the sulphate of copper, and uniting in its precipitation with a portion of the latter *.

Arsenic is employed in several arts. In the state of the white oxide it is used in the manufacture of glass to give it more transparency, and, in a larger quantity, a milky opacity. It is an ingredient in several processes of dyeing, and some of its preparations are used as paints. It is sometimes employed in the practice of medicine.

From oxide of arsenic being employed as a poison, it is often of importance, in cases of judicial investigation, to

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* Scheele's Chemical Essays, p. 253.

have tests by which it can be recognised. These chemistry is capable of furnishing.

The stomach having been removed, its contents carefully collected and washed out, are to be diffused in water, that the lighter materials may be removed, and any arsenic, which from its greater specific gravity will subside, be obtained. The matter which had been previously rejected by vomiting, may be examined in a similar manner. It is only when the arsenic is thus procured in substance, that the tests can be applied with certainty, for when dissolved and mixed with the fluid of the stomach their operation is ambiguous, or they fail in discovering it. If a very small quantity however be procured, all the necessary trials may be made; for this purpose it should be subdivided, if possible, into three or four portions, on which the experiments may be performed.

1*st*, A little of the substance obtained, supposing it to be arsenic, may be mixed with about an equal weight of black flux, or if this cannot be procured, with half its weight of charcoal powder, and exposed to a low red heat in a glass tube, coated with clay and sand, and stopt with a plug of clay. The oxide will be reduced, and, the metal being volatilized, will form a brilliant crust on the internal surface of the tube. It may be reserved for other experiments. This test is the most decisive of any; it is indeed perfectly so; and the only disadvantage attending it is, that it is not the most delicate, as it can only be properly employed when at least a grain of the oxide of arsenic can be operated on.

2*d*, If a small quantity of the reduced metal in powder, or a little of the white oxide, mixed with half its weight of charcoal, and made into a soft paste with oil, be placed between two clean pieces of copper, securing them by iron wire twisted round; after exposure of the pieces to a red heat for ten minutes, they will, when washed and rubbed with a little soft chalk, be found permanently whitened on the surfaces which had been in contact with the arsenic. This test is not a very delicate one, the white colour not being very well marked, unless a grain or two of the oxide has been employed. It is also necessary to attend to the circumstance, that the copper, by the mere agency of the heat and charcoal alone, may acquire a greyish or light yellow colour: this is easily distinguished, however, from the white colour produced by the arsenic.

3d, A minute quantity of the oxide may be put on a piece of iron and heated: it will evaporate in a white smoke before the iron is red-hot. If, before being exposed to heat, it is made into a paste with oil, it will, when evaporating, give the peculiar smell resembling that of garlic, which arsenic in vapour has. Or a little of the reduced metal heated in a similar manner, will be volatilized with the same odour. This test, however, is the least certain one. Other substances, not very different in appearance from oxide of arsenic, may be volatilized when placed on a hot iron; and though the peculiarity of the arsenical odour has been much relied on, there is perhaps some room for fallacy, not only from the difficulty of judging of it with accuracy, and so as to guard against imagination, but also, as some other metals, particularly antimony, have been supposed in volatilizing to give an odour, more feeble indeed, but somewhat similar.

4th, If a grain of the oxide be dissolved with twice its weight of carbonate of potash, in about two drachms of warm water; on adding this solution to a warm solution of five grains of sulphate of copper in a similar quantity of water, a precipitate of a lively grass-green colour will be formed. This is a very delicate test. At the same time it requires care in its application. A solution of carbonate of potash alone throws down a green precipitate from sulphate of copper, when a certain quantity of it is added. This however is a bluish green, and has none of the grass-green tint of the other. For greater certainty both solutions, that of the carbonate with the oxide, and that of the carbonate of potash alone, of the same strength, ought to be added to separate portions of the solution of sulphate of copper; the difference will then be perfectly evident; the experiment, too, ought to be made in day light.

5th, Another test proposed by Mr Hume, is that of nitrate of silver. If a piece of the common fused nitrate, or lunar caustic, be applied to the surface of a solution prepared by boiling the white oxide with an equal weight of carbonate of soda in a large quantity of water, a precipitate of a bright yellow colour is instantly formed. A similar test had been proposed by Dr Marcet. A rod of glass, dipt in a solution of ammonia, is applied to the surface of any liquor suspected to contain oxide of arsenic dissolved, and a similar rod dipt in a solution of nitrate of silver is then applied. If even a very minute quantity of arsenic is present, a precipitate of a lively yellow colour falls down *. This test is perhaps the most delicate of any, the effect being most distinct when not more than a grain of the oxide is contained in ten ounces of water; the first mode of applying it is most easily managed. Additional certainty may be given, if a sufficient quantity of the yellow precipitate be obtained, by drying it, mixing it with half its weight of potash and of charcoal powder, and exposing the mixture to heat in a glass tube. A crust of metallic arsenic will be obtained if the experiment, which is somewhat difficult, be properly conducted.

These two last tests admit of being applied to the liquid found in the stomach. They are then, however, liable to fallacy. If any matter, for example, which is of a yellowish colour, or which is liable to acquire that colour from the action of an alkali, such as certain vegetable infusions, be present, this may give a green tinge to the blue precipitate

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* Medico-Chirurgical Transactions, vol. ii. p. 156. Nicholson's Journal, vol. xxxiv. p. 174.

of oxide of copper, especially while it remains diffused, and thus produce an effect somewhat similar to that considered as an indication of oxide of arsenic. With regard to the other it has been found, that phosphoric acid, either free, or in any soluble saline combination, gives a yellowish precipitate with nitrate of silver, which may be mistaken for that from the presence of oxide of arsenic; and its presence occasionally in the contents of the stomach is by no means improbable. These fallacies, it is obvious, apply only in the application of the tests to the liquid of the stomach. If any powder of sparing solubility has been obtained, and is operated on in a state of solution in water, there can be no uncertainty.

It is also obvious, that any difficulty exists only where a very small quantity of arsenic has been obtained. With larger portions all the results may be obtained free from fallacy, and the first alone may be rendered decisive.

CHAP. XVII.

COBALT.

The ores of cobalt had been used for a property which they have of giving a deep blue colour to glass, but the metal was unknown until it was obtained by Brandt, a Swedish chemist, in 1732. Bergman more fully investigated its properties.

Cobalt occurs in nature alloyed with other metals, and mineralized by oxygen, and by arsénic acid. On a large scale it is extracted in the state of an oxide. The ore is roasted, by which the sulphur and arsenic are expelled, and any fusible metal is melted out. The cobalt remains in the state of an impure oxide, named Zaffre. The zaffre of commerce is always mixed with siliceous earth; hence, if exposed to a strong heat, it vitrifies, and a glass of a dark blue colour is formed, named Smalt, which is used on account of its colour in various arts.

It is from the zaffre of commerce that the chemist obtains cobalt. The common process is to mix the zaffre with three times its weight of black flux, a small quantity of oil, and a little sea-salt, and expose the mixture in a crucible to a strong white heat for some hours. A button of cobalt is obtained, on cooling, at the bottom of the crucible, generally alloyed, however, with arsenic and nickel, and sometimes with other metals, particularly iron. Processes have been given by different chemists to obtain it pure, as by Lampadius *, Tassaert †, Trommsdorff ‡, Bucholz ||, and Richter §. That by Trommsdorff may be selected. "Four parts of zaffre well pulverized are to be mixed carefully with one part of nitre, and half a part of charcoal in powder: this mixture is to be projected in small quantities into a red hot crucible, and this operation repeated three times, adding each time to the residue new portions of the nitre and the charcoal. The mass resulting from these detonations is to be mixed with one part of black flux, and exposed during an hour in a crucible to a red heat. The metallic matter is to be separated, pulverized, mixed with three times its weight of nitre, and the mixture again deflagrated. The iron thus becomes strongly oxidated, and the arsenic acidified combines with the potash: the mass pulverized is to be repeatedly lixiviated, and the liquor filtered; the arseniate of potash is

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* Annales de Chimie, tom. xxvi. p. 89.

† Ibid. tom. xxviii. p. 92.

‡ Nicholson's Journal, vol. xii. p. 258.

|| Philosophical Magazine, vol. xxiii. p. 195.

§ Annales de Chimie, tom. liii. p. 107.

thus separated from the insoluble residue that contains the cobalt. This residue is to be treated with nitric acid, which dissolves the cobalt without attacking the iron oxidated to its *maximum* of oxidation. The solution is then to be evaporated to dryness, the residue re-dissolved in nitrous acid, and the liquor filtered. The nitrate of cobalt is to be decomposed by potash, the precipitate washed and reduced by charcoal with heat *." This process is perhaps defective, if nickel be present; but the oxides of nickel and cobalt may be separated, according to the method of Thenard or that of Phillips, to be immediately stated under the history of nickel.

In the purest state in which cobalt has been obtained, it is of a white colour, inclining to grey; and, if tarnished, to red: it has a moderate degree of lustre: its fracture is compact, and of a fine grain: it is hard and brittle, though at a red heat it has a degree of malleability. Its specific gravity is 7.8, or according to some statements 8.5.

Cobalt appears to be possessed of magnetic power. Gren remarked, that the purest cobalt is not only attracted by the magnet, but that, according to the experiments of Wenzel, it is capable of acting as a magnet. This has been confirmed by Tassaert, who found, that cobalt which had been subjected to processes by which any iron must have been abstracted, and which shewed no trace of that metal, by tests by which a very minute portion of iron added to it was discovered, was as much attracted by the magnet as iron †.

Cobalt is very infusible: in the heat of a wind-furnace, it can, however, be brought into perfect fusion. Its melting point was estimated by Guyton at 130° of Wedgwood. By slow cooling, it is obtained in imperfect prismatic crystals.

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* Nicholson's Journal, vol. xii. p. 248.

† Annales de Chimie, tom. xxviii. p. 102.

When heated strongly in contact with the air, it suffers oxidation: its oxide is of a blue colour, and as the heat is continued deepens, and at length appears black. The precipitate thrown down from the salts of cobalt by the alkalis, is of a blue colour, and was regarded by Thenard [*] as the metal in the first degree of oxidation; it is probably a hydrate or a sub-salt. It dissolves in acids without effervescence. By exposure to the air, it appears to absorb oxygen: it assumes an olive colour, and, when dissolved in muriatic acid, with the assistance of heat, forms oxymuriatic acid gas. When dried, by exposing it to heat in contact with the air, it acquires a brown colour, which deepens until it become black; and in this change, according to Thenard, it absorbs more oxygen, as, when dissolved in muriatic acid, it forms a large quantity of oxymuriatic acid gas. According to Proust, the oxide at the maximum of oxidation contains 0.26 of oxygen, that at the minimum 19 [†]. According to Rolhoff, the protoxide is composed of 100 of metal, with 27.3 of oxygen; the per-oxide of 100 with 40.95. Some chemists supposed, that by saturation with oxygen, cobalt is brought to the state of an acid; but this cobaltic acid, the existence of which was announced by Brugnatelli [‡], has been proved, by the experiments of Darracq [||], and of Bucholz [§], to be arsénic acid, with a little oxide of cobalt.

A number of the acids oxidate cobalt, and combine with its oxide.

The concentrated sulphuric acid scarcely acts on it in the cold, but, when boiled on the metal, sulphurous acid gas is disengaged, and a saline matter is obtained, which, when lixiviated, forms a solution of sulphate of cobalt.

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[*] Annales de Chimie, tom. xlii. p. 210.

[†] Philosophical Magazine, vol. xxx. p. 341.

[‡] Ibid. vol. vi. p. 227.

[||] Ibid. vol. xii. p. 49.

[§] Ibid. vol. xviii. p. 97.

This, when concentrated, is of a reddish colour: when green, it denotes the presence of nickel. By evaporation crystals are obtained, acicular, or rhomboidal tetraedral prisms bevelled on the extremities. These are of a reddish colour. This salt is decomposed by heat, and, when urged by a strong fire, affords a black oxide.

Nitric acid is decomposed by cobalt, and the metal is oxidated and dissolved. The solution is of a red colour, and affords minute prismatic crystals of the same colour, which are deliquescent and decomposed by heat.

Muriatic acid does not act on cobalt but with the assistance of heat; a small portion of the metal is dissolved: the oxide is dissolved more readily: this solution is of a reddish colour, and by slow evaporation affords needle-like crystals, which are deliquescent. A similar solution is obtained by the action of nitro-muriatic acid on cobalt, or on zaffre. The solution of muriate of cobalt, according to Proust, is blue, and it is only when the oxide is in the state of what he names Hydrate, or combined with water, that it is red. Metallic cobalt in filings inflames when heated in oxymuriatic gas.

The solution of muriate of cobalt affords a celebrated sympathetic ink. For this purpose it is prepared either by digesting nitro-muriatic acid on zaffre with a moderate heat, and diluting the solution as far as can be done, so as to admit of the green colour being produced by heat; or by digesting zaffre with diluted nitric acid, diluting with twenty-four parts of water, and adding as much muriate of soda, as there has been zaffre employed. Letters traced on paper with this dilute solution, and allowed to dry, are invisible; but when the paper is exposed to a moderate heat, they appear of a lively green: they disappear again when cold; and the experiment may be repeated any number of times, taking care only to avoid too strong a heat, by which they are rendered permanent. This phenomenon has been ascribed to the muriate of cobalt fixed upon the paper, attracting moisture from the atmosphere, by which it is as it were dissolved and rendered invisible: when heated, this moisture is evaporated, and the green colour of the salt appears. This explanation appears to be confirmed by the fact, that the characters are rendered visible by confining the paper in a vessel with quicklime, or sulphuric acid, either of which attracts humidity powerfully. The green colour cannot, however, be ascribed entirely to the concentration, but is owing to the temperature; for the solution itself becomes green when heated in a close phial, and loses this green colour as it cools. It is not easy to explain how the temperature does produce this change of colour. Mr Hatchet suggested, that it may operate by causing "a temporary difference to take place in the proportions of oxygen existing in the acid menstruum and the oxide [*]," but similar changes of colour are produced in many cases by the action of heat alone, where this supposition cannot be applied, as has been shewn, in an extensive series of experiments by Gay Lussac [†].

A blue or purple sympathetic ink is said to be formed, by boiling one part of pure oxide of cobalt in sixteen parts of distilled vinegar, and evaporating the solution to one-fourth of the whole. The fluid is filtered, and is again evaporated to one-half. Muriate of soda, to the amount of one-fourth of the cobalt, is dissolved in it, and the solution strained. And a weak red sympathetic ink may be made by dissolving pure oxide of cobalt in pure acetic acid, and diluting the solution with water. I have observed, that the solution in nitric acid exhibits a rose-colour when paper is heated on which lines are impressed with it, but it requires more heat to produce the effect than the muriate does to produce the green colour.

The actions of the other acids on cobalt have not been

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[*] Philosophical Transactions, 1796, p. 333.

[†] Philosophical Magazine, vol. xli. p. 450.

minutely examined. Phosphoric acid dissolves its oxide, and forms a red-coloured solution, which becomes turbid as the solution is saturated, probably from the sparing solubility of the salt. Fluoric acid dissolves the oxide, forming, according to Scheele, a gelatinous solution; which, according to Fourcroy, yields crystals by evaporation. Boracic acid forms a compound of sparing solubility, which is precipitated when a solution of borate of soda is added to a solution of nitrate of cobalt. By a similar process, the carbonate of cobalt is formed, which is likewise insoluble.

The solutions of the salts of cobalt are decomposed by the alkalis, and precipitates thrown down of a red tinge, or of a blue colour, if the cobalt is pure. By an excess of alkali, these are re-dissolved. This is more particularly the case with ammonia: the solution is of a deep red colour if there is an excess of ammonia; it is decomposed very sparingly by potash, and even when the excess is evaporated, the decomposition is slow and imperfect: the solution, on the addition of the potash, changes from red to pink, then to brown, and at length deposites brown oxide of cobalt *. According to Thenard's experiments †, it is the blue oxide only that is soluble in ammonia; the black being not sensibly dissolved. The ternary salt, obtained by adding to nitrate of cobalt, ammonia in quantity sufficient to re-dissolve the precipitate, may be obtained by evaporation in small cubes of a red colour, which are permanent in the air, and are decomposed by heat ‡.

Cobalt does not combine with sulphur by fusion, but it combines with the alkaline sulphurets; the compound is of a white or yellowish colour, and a crystalline texture. Hydro-sulphuret of potash throws down a black precipi-

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* Philosophical Magazine, vol. xvi. p. 314.

† Ibid. vol. xx. p. 66.

‡ Annales de Chimie, tom. xlii. p. 215.

tate from the solution of nitrate or muriate of cobalt, which, by an excess of the hydro-sulphuret, is re-dissolved *. Oxide of cobalt, heated with sulphur, produces, according to Proust, a sulphuret in which about 40 of sulphur are combined with 100 of the metal.

When small pieces of phosphorus are projected on cobalt ignited in a crucible, the cobalt is fused, from combining with the phosphorus, and forming a compound more fusible than the metal; it thus absorbs about one-fifteenth of its weight. A similar compound is obtained by fusing together cobalt, concrete phosphoric acid, and a little charcoal. The phosphuret is of a white colour, with metallic lustre, which is impaired on exposure to the air: it is brittle, and of a striated fracture. Urged by the flame of the blowpipe, the phosphorus is burnt out, and a blue oxide of cobalt remains, forming, with a portion of the phosphoric acid, a vitreous globule.

Cobalt combines with many of the metals. Its alloys are generally brittle, and none of them has been applied to any use; nor have they been much examined. That with gold, in which the cobalt is only one-fifteenth of the mass, was found by Mr Hatchet to be of a dull yellow colour, and very brittle: it was brittle even when the proportion of cobalt amounted only to $\frac{1}{63}$. The combination with silver is not easily effected, and is modified by the relative quantities; hence, when they are fused together, on cooling, the upper part of the mass is principally cobalt, which, being whiter than usual, appears to have a little silver combined, while the other is principally silver, which, from being brittle and of a grey colour, appears to have a portion of cobalt in combination. The relation of cobalt to platina is not known. It cannot be united with quicksilver. With copper it has been said to form an alloy of a white colour, hard and brittle; but this, as indeed many

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* Annales de Chimie, tom. xxviii. p. 104.

of the observations with regard to the alloys of cobalt, applies only to the metal in its impure state. The affinity of cobalt to iron has been considered as very powerful, from the difficulty of separating them, though the opinion with regard to this difficulty appears to have arisen from the supposition, that the magnetic quality of cobalt depends on iron. Iron and cobalt, however, combine together, forming an alloy of a close grain, and very hard. It had been supposed, that cobalt does not unite with lead; but, from the experiments of Gmelin, it appears, that they can be combined in different proportions, by exposure in a covered crucible to the heat of a forge. Equal parts formed an alloy, having more resemblance to cobalt than to lead, brittle, and of the specific gravity 8.12. With two parts, and even with four parts of lead, and one of cobalt, alloys were formed, brittle, and harder than lead; with six parts of lead it was more malleable: with eight parts its malleability was equal to that of lead, and its hardness greater: its specific gravity was 9.78 *. The alloy with tin is said to be of a close grain, and of a violet colour. Cobalt does not combine with zinc. With nickel it is often naturally united: the alloy that may be artificially formed has not been examined.

The principal use of cobalt, is to communicate a blue colour to glass, enamel, and porcelain. For this purpose it is used in the state of oxide. Smalt, which is the oxide vitrified with siliceous earth, is from its deep blue colour sometimes used as a pigment, and is also employed to give a bluish tinge to linen, or lessen its yellow shade.

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* Annales de Chimie, tom. xix. p. 359.

CHAP. XVIII.

NICKEL.

An ore named Kupfer-nickel, had been known to mineralogists, without its particular nature having been discovered, until Cronstedt, in 1751, shewed that a metal can be extracted from it, different in its characters from every other. To this the name of Nickel was given. As it has a resemblance in some of its properties to copper, and is also magnetic, it was regarded by some as an alloy of copper and iron, with a portion of arsenic. Bergman undertook the investigation of its properties, and, though he found it extremely difficult to obtain it pure, he established its claim to be ranked as a peculiar metal.

The species of nickel ores are, its alloy with arsenic with a little sulphur, Kupfer-nickel, as it is named, and its oxide. It is from the former that the metal is extracted, but it is difficult to free it entirely from the other metals with which it is associated. The process of Cronstedt was to expel the volatile principles by roasting; and the residual matter being mixed with two or three times its weight of black flux, and melted in a forge, a metallic button was obtained, composed of the nickel alloyed with arsenic, cobalt, and iron. Bergman endeavoured to obtain it pure by various processes,—as by repeated calcinations and scorification;—by fusing it with sulphur and borax, or with an alkaline sulphuret; by repeated scorification with nitre; and in the humid way, by solution in nitric acid, and reduction of the nitrate, or decomposition of it by potash, and re-dissolving the precipitate in ammonia: but he could scarcely obtain it free from arsenic;

and after all his trials he found reason to conclude, that it is scarcely possible to obtain a complete purification of nickel *. Other methods have since been employed, by different chemists, as by Klaproth †, Chenevix ‡, Philips §, Thenard ||, Bucholz ¶, and Richter **. The process given by Chenevix is the most simple. The metal obtained from kupfer-nickel by the process of Cronstedt is dissolved in nitric acid, the solution being boiled, so that the arsenic present may be converted into arsénic acid: a solution of nitrate of lead is dropt in, and the liquor is evaporated by a very gentle heat, but not quite to dryness. Alkohol poured into this solution precipitates every salt but the nitrate of nickel which has been formed by the double decomposition of the arseniate of nickel and the nitrate of lead. The alkohol of the solution of nitrate of nickel being evaporated, the metallic salt is re-dissolved in water, and decomposed by potash; and the oxide, well washed and dried, is reduced in a Hessian crucible lined with lamp black. In the process followed by Thenard, which appears well adapted to remove every foreign metal, the impure nickel being roasted until it ceases to exhale arsenical vapours, is dissolved in nitric acid; during the solution, the bismuth it contains is separated in combination with arsénic acid, in an insoluble powder. To the solution, sulphuretted hydrogen is added, by which the copper is precipitated. To separate the remaining arsenic, the solution is saturated with potash, and the metallic oxides existing in the solution are precipitated: though part of the arsenic is retained in the state of acid,

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* Chemical Essays, vol. ii. p. 257.

† Kirwan's Mineralogy, vol. ii. p. 459.

‡ Nicholson's Journal, 8vo, vol. iii. p. 287.

§ Philosophical Magazine, vol. xvi. p. 512.

|| Ibid. vol. xx. p. 65. ¶ Ibid. vol. xxiii. p. 193.

** Annales de Chimie, tom. liii. p. 164.

in combination with the potash, a part is also contained in the precipitate. It is therefore re-dissolved in nitric acid, and into this solution an excess of hydro-sulphuret of potash is poured: the arsénic acid remains in the liquor combined with the alkali, while the other oxides are precipitated in combination with sulphur and sulphuretted hydrogen: these are the oxides of nickel, cobalt, and iron: they are put into a matrass with nitric acid, and a solution is obtained, from which the pure oxides are again precipitated by potash. And, lastly, to separate them from each other, they are agitated with oxymuriate of lime: they thus pass to the maximum of oxidation. Oxide of nickel in this state is soluble in ammonia, while the oxides of iron and cobalt are not. Liquid ammonia being applied, therefore, a solution of the pure oxide of nickel is formed; and the ammonia being volatilized by heat, it is obtained of a beautiful green colour, and is reduced by exposure to heat in a Hessian crucible, mixed with oil, lamp black, and borax.

Nickel had been placed among what are named the Semi-metals, from appearing to have little ductility or malleability. This is owing, however, to the intermixture of other metals, particularly of arsenic, or to the combination of a little charcoal: more recent researches, particularly those of Richter, having shewn, that when pure, it is both ductile and malleable. It may be forged into very thin plates, their thickness not being greater than 0.01 of an inch, and it can be drawn into very fine wire. Its colour is white, intermediate between that of silver and platina, and is not altered by the air. It takes a fine polish, and is not liable to tarnish or rust. Like steel, it assumes different superficial colours when heated. It is nearly as hard as iron. Its specific gravity is 8.279, and when forged 8.666 *.

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* Annales de Chimie, tom. liii. p. 173.

By the experiments that have been made on nickel in it's pure state, it is proved to be possessed of magnetic power. This property had often been observed in it; but as, in the usual processes by which it is obtained, it is alloyed with iron, it was concluded, with probability, that the magnetism it exhibited was owing to the presence of this metal. Since methods, however, have been discovered of obtaining nickel in a purer state, the error of this conclusion has been discovered. The magnetic property is found in it when there are no traces of iron, and instead of being weaker as the nickel is purified, which it ought to be did it depend on any intermixture, it becomes stronger, and is nearly equal to that of iron; so much so, that, as Thenard has observed *, if it depended on iron, the nickel must be supposed to contain half its weight of that metal, while not the least trace of it is discovered by re-agents, which can discover it if it were present to the amount of one hundredth of the mass. Mr Chenevix at one time concluded, that when nickel is freed from iron, it is not magnetic; but he afterwards discovered, that the loss of the magnetic property was owing to the presence of arsenic †. Nickel, therefore, must be allowed to be magnetic. The effect of the magnet on it is little inferior to that on iron: and the metal itself becomes magnetic by friction with a magnet, or even by beating it with a hammer ‡: it's magnetic energy is to that of iron, according to Lampadius, as 35 to 55. Magnetic needles have been constructed of it, and have been preferred to those of steel, as resisting better the action of the air. The nickel preserves its magnetic property when alloyed with copper, though it is somewhat diminished: by a small portion of arsenic, it is destroyed. A slight degree even of oxidation like-

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* Philosophical Magazine, vol. xx. p. 69.

† Nicholson's Journal, 4to, vol. v. p. 287.

‡ Annales de Chimie, tom. liii. p. 175.

wise impairs it, as does also, according to Tourte, the application of heat.

Nickel is extremely infusible; its fusing point being higher than that of iron. Thenard, in reducing its oxide, was unable to melt the metal completely in the heat of a forge, in which a Hessian crucible began to fuse, and in which malleable iron was melted without any addition: he obtained only metallic globules, interspersed in a mass imperfectly agglutinated [*]. The experiments of Richter [†] agree as to the difficult fusibility of nickel with those of Thenard; if in other experiments it has appeared more fusible, this has been owing to the alloy of other metals. In Thenard's experiments, nickel appears to have been even volatilized, metallic particles adhering to the cover of the crucible. Its power of conducting heat is considerable.

This metal is oxidated by exposure to atmospheric air at a high temperature, though with difficulty. It loses its lustre, and becomes of a brown colour. According to Tourte, it burns when heated in oxygen gas. Its oxide is more easily obtained by exposure to heat with nitre; it is of an apple-green colour, and is obtained of this colour by precipitation from some of its saline combinations: as, for example, from the nitrate decomposed by potash, the precipitate being washed and submitted to a heat inferior to ignition. This green oxide contains, according to Tupputi [‡], 100 of the metal with 27 of oxygen; according to Rolhoff, 100 with 27.3 [||]. According to the experiments of Thenard, another can be formed more highly oxidated by exposing the green oxide to a red heat, or by treating it with oxymuriatic acid, or oxymuriate of lime. It is of a black colour, and is soluble in sulphuric and nitric acids,

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[*] Philosophical Magazine, vol. xx. p. 68.

[†] Nicholson's Journal, vol. xii. p. 77.

[‡] Annales de Chimie, tom. lxxxviii.

[||] Davy's Chemical Philosophy.

with a disengagement of oxygen *. It appears, therefore, to be too highly oxidated to be capable of directly combining with acids. It consists, from Rolhoff's estimate, of 100 of metal with 40.95 of oxygen. According to Richter †, oxide of nickel is reduced by heat alone; and the only difficulty in this reduction is the intensity of the heat required to fuse the metal.

Nickel is dissolved by a number of the acids; its solutions are of a green colour, and crystallizable.

Sulphuric acid acts very weakly on nickel: when boiled on it, sulphurous acid is disengaged, and a grey coloured mass remains, partly soluble in water, and communicating to it a green tinge: by evaporation of this solution, or of that of the oxide of nickel in sulphuric acid, crystals in tables, or in short prisms, of a pale emerald-green colour, are obtained.

Nitric acid acts rapidly on impure nickel: when the nickel is pure, the action is very moderate, and requires the assistance of heat. The solution is of a rich green colour, and by evaporation affords rhomboidal crystals, which, according to Bergman, are deliquescent, and by long exposure to a warm air lose their acid. It is partially decomposed by heat.

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* Philosophical Magazine, vol. xx. p. 67.

† Richter, in reducing the precipitate from a solution of nickel, obtained only metallic globules, interspersed in scorified matter of a black colour. In some subsequent experiments, (Nicholson's Journal, vol. xii. p. 262.), he found that this matter could not be reduced by heat alone, but only when in mixture with charcoal powder. The metal obtained was of a grey colour, hard and brittle, magnetic, but less so than iron or nickel, more fusible than nickel, and resembling it in many of its properties, but differing in others. He regarded it as a different metal, and gave it the name of Nickeline. Hisinger has shewn, that it is an alloy of nickel with cobalt, a little iron, and a trace of arsenic, (Annals of Philosophy, vol. i. p. 116.).

Muriatic acid acts feebly on nickel, so that the best mode of removing any crust from the surface of nickel, is to boil it in this acid, which dissolves scarcely any of it: it dissolves its oxide, however: the solution is green, and by evaporation affords crystals, which are deliquescent. When the metal is heated in oxymuriatic gas, an olive coloured substance is formed.

Phosphoric acid not only does not act on nickel, but, according to Bergman, scarcely dissolves any of its oxide, the liquor affording no crystals, and being scarcely green. The Fluoric acid combines with the oxide, and forms with it a salt, which can be obtained in crystals of a pale green. The Boracic acid does not immediately combine with it; but the combination may be effected by the exertion of a double attraction. Carbonic acid may be combined with the oxide of nickel by a similar method,—adding to the solution of nitrate of nickel a solution of carbonate of potash; a precipitate of carbonate of nickel is formed of a rich apple-green colour; 2927 parts are obtained, according to Richter, from 1000 parts of nickel. When exposed to heat, its colour changes to a dark grey, with scarcely any green tinge, and with a considerable loss of weight: if urged by a strong heat, it approaches more and more to the metallic state, and the small grains are at length attracted by the magnet *.

The salts of nickel are decomposed by the alkalis, and the oxide, more or less free from acid, is thrown down. If the alkalis are added in excess, they re-dissolve it; and with ammonia in particular, soluble triple salts are formed. Potash and soda dissolve even a small quantity of its pure oxide: ammonia dissolves it in larger quantity. From the experiments of Thenard, it appears, that it is the green oxide which is soluble in ammonia, and that the black oxide, in being acted on by that alkali, is reduced to the

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* Nicholson's Journal, vol. xii. p. 80.

state of green oxide; its excess of oxygen combining with the hydrogen of part of the ammonia, and nitrogen gas being disengaged[*]. The solution of the oxide of nickel in ammonia is of a rich blue colour, similar to that of oxide of copper; but what peculiarly distinguishes it is, that it gradually changes to a purple, and lastly to a violet: the violet colour is, by the addition of an acid, changed to a green; but, by the addition of ammonia, the original colour is re-produced. These changes of colour, Richter points out as characteristic of pure nickel[†]. The solution of oxide of nickel in ammonia is decomposed, according to Mr Phillips, by the addition of soda or potash; and he has pointed out this as affording a certain and easy method of obtaining, what is otherwise very difficult, nickel free from cobalt; the oxide of the latter, when dissolved in ammonia, being slowly and sparingly precipitated by potash, while that of the former is precipitated immediately and largely[‡]. He ascribes these decompositions to the two alkalis combining, and thus weakening the affinity of either to the metallic oxide.

Nickel combines with sulphur by fusion. The compound has a yellow or grey colour, with some brilliancy: it is brittle and hard, and burns when strongly heated in the air: 100 of the metal combine, according to Lampadius, with 10 of sulphur, and by this its magnetic power is destroyed[||]. Nickel is also dissolved by the alkaline sulphurets. Its salts are not precipitated by sulphuretted hydrogen.

With phosphorus nickel unites, either by projecting the phosphorus on the nickel at a high temperature, or by heating together phosphoric acid and nickel with a little charcoal. The nickel increases in weight one-fifth, or,

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[*] Philosophical Magazine, vol. xx. p. 67.

[†] Nicholson's Journal, vol. xii. p. 80.

[‡] Philosophical Magazine, vol. xvi. p. 514.

[||] Annals of Philosophy, vol. v. p. 61.

according to Lampadius, one-seventh. The compound is of a white colour, with metallic lustre, and appears composed of a congeries of prisms: is hard and very brittle, and the magnetic quality is entirely lost.

Nickel forms alloys with a number of the metals, but our knowledge of these combinations is very imperfect. Bergman only has given some slight notices with regard to them; and these cannot be relied on, as he never obtained nickel free from alloy. Nickel, he observes, when impure, does not unite with silver; "but this must be attributed to the cobalt it contains; for when well freed from that metal, it easily unites in equal proportions with the silver, and that without any remarkable diminution either of whiteness or ductility. This mixture, fused with borax, tinges it of a hyacinthine colour. Copper unites more slowly with purified nickel, yielding a red and ductile metallic mass, which tinges borax of a reddish hyacinthine colour. With an equal, or a greater bulk of tin, nothing is produced but a brittle mass; in which respect also nickel differs from cobalt. It could not be amalgamated with mercury by trituration. Purified nickel melts with tin, and forms a brittle compound *." Nickel, Mr Hatchet found, impaired greatly the ductility of gold; but this might be owing to its not being free from arsenic, as, from its ductility in its pure state, we might conclude that it would not lessen much this quality in gold; and accordingly, Lampadius states that the alloy is malleable and hard. With platina nickel combines, according to Lampadius, when they are heated on charcoal by oxygen gas; the alloy is completely malleable, acquires a fine polish, and has a yellowish white colour, not unlike silver; it retains the magnetic quality. The combination with silver appeared, from his experiments, to be very imperfect. With copper it combines easily, and, what is rather singular, though both metals

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* Chemical Essays, vol. ii. p. 272.

are ductile, the alloy is brittle; it exhibits no trace of magnetism. With iron it unites, forming an alloy of considerable lustre, and of a white colour, little liable to rust; and it is singular, that native iron, occurring in what are called Meteoric Stones, is always alloyed with nickel.

The oxide of nickel can be combined by fusion with the vitrifiable earths, and gives to the glasses they form a hyacinthine colour. It gives a similar colour to borax, and to phosphate of soda.

Nickel has not hitherto been applied to any use; but were a simple and economical process for purifying it discovered, it might, from the qualities it possesses, be applied to many purposes of utility. It has been applied to the fabrication of magnetic needles, and has the advantage over iron of not being liable to rust.

CHAP. XIX.

MANGANESE.

The ores of manganese had, from their external characters, been confounded with those of iron. Bergman and Scheele first regarded the native oxide of manganese as containing a peculiar metal, and this metal was obtained by another Swedish chemist, Gahn. At rather an earlier period, Dr Irvine had formed the same conclusion with regard to it, and had examined some of its properties*. The name Manganese, formerly given to the native oxide, is now appropriated to the metal.

There are two species of manganese ores,—the black, in which it is mineralized by oxygen, and the red, in

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* Preface to Dr Irvine's Chemical Essays.

which the oxide is combined with carbonic acid and silex. The latter is a rare, the former an abundant ore. The oxide of manganese occurs in small quantity in a number of other minerals; it exists also in the vegetable kingdom, being found generally in the ashes of plants. Metallic manganese is applied to no useful purpose, and is therefore not extracted from its ore on a large scale. The reduction of its oxide even in small quantity is difficult, partly from its strong attraction to oxygen, and partly from its great infusibility; nor has it been obtained but in globules. The process generally followed, is that originally given by Gahn,—selecting a pure native oxide of manganese, reducing it to powder, making it into a ball with a little oil, and exposing it imbedded in charcoal, in a covered crucible, to a very intense heat gradually raised. To obtain it with more certainty free from iron, it may be proper, instead of operating on the native oxide, to dissolve this in nitric acid, adding a little sugar, which promotes the solution: this solution is to be decomposed by carbonate of soda: the white precipitate that is thrown down, is carbonate of manganese, which may then be reduced in the same mode. Other methods more complicated were given by Kirwan, by which the iron may be abstracted *. Succinic acid precipitating the iron, affords the most simple mode of abstracting it from the manganese, but it is too expensive: oxalic acid was proposed by Dr John. Mr Hatchet has given a method more simple and effectual,—that of adding ammonia very slightly in excess to the muriatic solution; the oxide of iron is speedily precipitated †.

Manganese, when obtained in its metallic form, is of a white colour, with a shade of grey, and with moderate lustre. Its texture is granular: its hardness equal to that of iron. It appears to have neither ductility nor mallea-

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* Elements of Mineralogy, vol. ii. p. 460.

† Annals of Philosophy, vol. ii. p. 344.

bility. Its specific gravity is 6.850, or, according to another estimate, 8.013. It is not magnetic when entirely free from iron, but a small portion of this metal is sufficient to give it that property.

It has been observed, that the globules of metallic manganese, when exposed to the air, split, fall to pieces, and at length are converted to a brown powder. Yet other specimens are obtained, which are not liable to this change, preserving their metallic appearance unaltered. This difference Kirwan supposed owing to the former containing carbon, which absorbs oxygen, and subverts the cohesion of the metal *. The presence of a little iron has been said to prevent this effect. According to Dr John, the falling down into powder from the action of air is a property of pure manganese; and it remains unaltered when it is alloyed with a little copper or iron.

The melting point of manganese can scarcely be estimated with precision. It is supposed by Guyton to be at least 160° of Wedgwood.

Exposed to heat in contact with the air, it passes rapidly through different stages of oxidation, assumes a grey colour, which passes to a yellow, red, and brown, and at length becomes black. By precipitation by an alkali from some of its saline combinations, it is obtained also in the state of an oxide, or rather an hydrated oxide, white, or of a yellowish colour approaching to white. The black oxide is evidently the metal at the *maximum*, in the other it is probably at the *minimum* of oxidation. These were regarded as the two definite oxides of the metal. According to Bergman, the white oxide consists of 80 of manganese, and 20 of oxygen: the black oxide was stated by Fourcroy to be composed of 60 of manganese, and 40 of oxygen. The subject has since been more minutely investigated, and is not altogether determined.

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* Elements of Mineralogy, vol. ii. p. 288.

Dr John, in an experimental investigation of manganese, inferred, that there are three oxides having fixed proportions of oxygen, a green, brown, and black. The first is obtained when water is decomposed by manganese at a high temperature, and contains 13 *per cent.* of oxygen. This exposed to the air, gains weight by absorption of oxygen, and forms a brown oxide, containing 20 *per cent.* of oxygen, and the oxide at the maximum obtained by the decomposition of the nitrate by heat, and analogous to the native black oxide, contains 28.67 of oxygen ; or in the three 100 are combined with 15, with 25, and with 40 *. Berzelius assumed the existence of five degrees of oxidation, the first constituting the grey powder, into which metallic manganese falls when exposed in an imperfect manner to the air, and in which 100 of metal are combined with 7.026 of oxygen ; the second the green oxide of John, composed of 100 with 14 ; the third an oxide which, from the analysis of the sulphate of manganese, is composed of 100 with 28 ; the fourth an oxide which, from analysis, he found to consist of 100 with 42.16 ; and the fifth the native oxide, which, according to calculation, is composed of 100 with 56.215 †. The first of these, however, was admitted to be doubtful ; the proportions in the last were only theoretically assigned ; and the results with regard to the others do not appear very certain. He accordingly subsequently omitted the first, and thus assigned four oxides, with the oxygen in the ratio 1, 2, 3, 4 ‡.

Sir H. Davy had concluded, that there are only two oxides of manganese. The first, of a dark olive colour, is obtained by exposing the white hydrate precipitated from the salts of manganese by an alkali, to a red heat without the contact of the air : it takes fire if heated

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* Annals of Philosophy, vol. iii. p. 417.

† Annales de Chimie, tom. lxxxiii. p. 169.

‡ Annals of Philosophy, vol. iii. p. 559.

in the air, increases in weight, and becomes brown, and it slowly absorbs oxygen even at common temperatures. The other, of a dark brown colour, is obtained when the first is exposed to a moderate heat with the admission of air; it also constitutes the native oxide, and by an intense heat it loses the additional proportion of oxygen, and is converted into the protoxide. The first, according to his experiments, is composed of 79 of manganese and 21 of oxygen, or 100 with 26.58; the second of 100 with 39.82 *.

Gay Lussac admits three oxides; the protoxide obtained in dissolving manganese in diluted sulphuric acid, and precipitating by an alkali without the admission of air; the deutoxide, obtained by calcining the peroxide, or the greater number of the salts of manganese; and the peroxide, which is found in nature, and may be obtained also from the action of chlorine on either of the others. Of these oxides the first and the third only are soluble in acids; the second always suffers a change of composition from the action of an acid, and is converted into the others †.

The existence of the oxide which is the base of the salts of manganese, and is obtained from them by precipitation by an alkali, and of the native or black oxide, as definite compounds, appears to be sufficiently established. The principal question to be determined is, whether the brown oxide, obtained by the partial decomposition of the peroxide by heat, is so or not? It does not appear, that by any intensity of heat, the entire conversion of the peroxide into the protoxide can be effected. The supposition, that the intermediate product is a mixture of the two, is altogether improbable; for since the whole mass can be raised to one temperature, there is no cause why one portion should remain different from the other. The opinion which has also been advanced, that it is a chemical compound of the other two oxides, is perhaps only a verbal

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* Chemical Philosophy, p. 567.

† Annales de Chimie et Physique, tom. i. p. 58.

distinction, or at least an hypothetical assumption, and is not established by the fact, that it is resolved into these two oxides by the action of an acid, since that action, it is obvious, may determine the formation of these from a definite compound of the two ultimate elements.

It has lately been stated, that Arvidson has established the existence of three oxides of manganese, composed of 100 of metal with 28, 42, and 56 of oxygen, with a compound intermediate between the first and second containing 37, and therefore not in the regular progression. But the results do not appear very clearly determined *.

The white hydrated oxide, obtained by precipitation by an alkali from the salts of manganese, contains, according to Sir H. Davy, about 24 *per cent.* of water, combined with the olive coloured oxide.

When manganese is in the lower degrees of oxidation, such as when it is precipitated from its saline combinations, it absorbs oxygen on exposure to the air, especially when in a humid state, or if dry, when it is heated; its colour deepens, and this proceeds until it is saturated with oxygen, and has become black. The black oxide, exposed to the heat of ignition, yields oxygen gas, in proportion as the heat is raised: but no degree of heat is able to reduce it to the state of the lighter coloured oxide: it can be brought no farther than the brown. By exposure to air, this brown oxide again deepens in its colour. The oxides of manganese are reduced by the operation of carbonaceous matter at a high temperature.

Metallic manganese decomposes water at the temperature of ignition, and evolves hydrogen gas, which has a peculiar smell, and burns with a green flame.

The action of the acids on metallic manganese has been little examined, as it is difficult to obtain it in this state; and as it must be oxidated in passing into any saline com-

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* Annals of Philosophy, vol. xi. p. 228.

binations, such combinations may equally be obtained by employing the oxidated manganese. In its metallic state, it is scarcely acted on by sulphuric acid ; but when the acid is diluted, hydrogen gas is disengaged, from the decomposition of the water, and the metal is oxidated and dissolved. Nitric acid dissolves it with effervescence, from the disengagement of nitric oxide gas. Muriatic acid dissolves it, hydrogen gas being evolved. Thrown into oxymuriatic acid gas, it is inflamed.

The relations of the oxides of manganese to acids were first examined by Scheele and Bergman *: and they present some important theoretical results. It appears that the black oxide is in too high a state of oxidation to be capable of combining with acids: it must be partially deoxidated, and this affords the explanation of the phenomena it presents with the acids.

Thus, when sulphuric acid is poured on the black oxide, and a moderate heat is applied to favour their mutual action, the acid and the oxide do not combine, but the oxide parts with a quantity of its oxygen, which assumes the elastic form, and then combines with the acid. The compound is soluble in water, and forms a solution of a red colour, having an excess of acid, which may be expelled by heat. On re-dissolving it, a solution is formed, which Bergman found to be not easily crystallizable, as, on evaporation, it becomes gelatinous, with a few crystals interspersed. It is deliquescent. The alkalis throw down from it a precipitate of a reddish yellow colour. Though in this combination the metal is less oxidated than it is in the black oxide, it is supposed not to be at the *minimum* of oxidation, but is in an intermediate state. This appears from its colour, and from the colour of the precipitate it affords, compared with that of the solution of the metal itself in sulphuric acid. This is nearly colourless; and, on slow evaporation,

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* Chemical Essays, vol. ii. p. 211.

affords crystals colourless, or of a pale rose colour, of a rhomboidal form: decomposed by the alkalis, it affords a white precipitate. A similar solution is formed, by adding the white oxide of manganese to diluted sulphuric acid; or by digesting the black oxide with sulphuric acid, and a small quantity of sugar, the carbonaceous matter of which de-oxidates the salt as it is formed, and reduces it to the state of the sulphate at the minimum of oxidation. Sulphurous acid, in acting on the black oxide, Scheele observed, forms a similar salt. The crystallized sulphate is soluble in 2½ parts of water; by a strong heat it is decomposed; it consists, according to Dr John, of 33.6 of acid, 31 of oxide, and 35.3 of water.

Sulphurous acid combines with the white oxide, and forms a sulphite, granular, insoluble, and permanent in the air. It contains 40 of oxide, and 60 of acid and water.

Nitric acid does not dissolve black oxide of manganese, from the same cause that the sulphuric does not,—the metal being in too high a state of oxidation. But nitrous acid, especially when highly fuming, acts upon it; the nitric oxide which this contains, abstracting part of the oxygen of the oxide, and thus rendering it soluble. Hence, as Scheele observed, any addition which can have the same effect, renders nitric acid capable of acting on the black oxide, as the addition of a little sugar or alkohol, or, what is an elegant experiment, exposing the acid to the rays of the sun, which converts the nitric into nitrous. A similar solution is formed, by adding the white oxide to nitric acid. In these combinations, the metal appears to be always at the minimum of oxidation: the solution is colourless, and, when decomposed by the alkalis, affords a white precipitate. The nitrate of manganese does not crystallize easily; but by a cautious evaporation, so as not to occasion decomposition, and sudden cooling, acicular crystals may be procured white, semi-transparent, and deliquescent.

Muriatic acid acts on black oxide of manganese, when aided by a moderate heat. This is owing to its power of combining with oxygen: hence, in this solution, equally as in the action of the other acids, the oxide is reduced in its degree of oxidation, a portion of the muriatic acid is converted into oxymuriatic acid, and the remaining acid combines with the oxide thus changed. It is in this way that oxymuriatic acid is generally formed; and it was in examining the action of muriatic acid on the native black oxide of manganese, that Scheele discovered that acid. The white oxide dissolves readily in muriatic acid, forming a solution similar to that obtained by the preceding process. By evaporation of the muriate of manganese, a soft deliquescent mass is obtained. It appears that manganese unites most readily with muriatic acid, when at a low degree of oxidation; yet a combination may be effected between them, when the metal is more highly oxidated; for when muriatic acid is allowed to remain with the black oxide, without applying heat, a portion of the oxide is dissolved, and the olution has a reddish colour. It has always an excess of acid, and, by dilution with water, is partially decomposed. Muriate of manganese crystallizes in four-sided tables of a rose-red colour, and transparent. They are rather deliquescent, and when heated undergo the watery fusion; they are decomposed by a red heat. Water and alkohol dissolve about their own weight of this salt. It consists of 38.5 of oxide, 20 of acid, and 41.5 of water. In oxymuriatic acid gas, metallic manganese when heated burns. The chloride, considering the compound as such, is best obtained by evaporating the white muriate to dryness, and heating the residue in a glass tube with the exclusion of air. A compound is obtained of a delicate pink colour, brilliant, and having a lamellar texture. It is represented by 46 of manganese, and 54 of chlorine *.

Phosphoric acid does not act on manganese, but com-

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* Davy, Philosophical Transactions, 1812.

bines with its oxides: the combination being effected by adding a solution of a neutral phosphate to a solution of nitrate or muriate of manganese. The phosphate of manganese is precipitated: it is white, insoluble in water, but soluble in weak acids as the acetous, and in these solutions is decomposed by the alkalis. By a similar process, the fluate and borate of manganese, which are likewise insolubie, are formed. Carbonic acid in solution in water, acts weakly on metallic manganese, dissolving a little of it, as it does also of the oxide; the solution deposites a pellicle of oxide, on exposure to the air, from the escape of the carbonic acid. The neutral carbonate is obtained by adding a solution of carbonate of potash or soda to a solution of muriate of manganese. When pure, and at the minimum of oxidation, it is of a white colour; if at a higher state of oxidation, it is yellowish or brown. The white carbonate consists, according to Dr John, of 55.9 of oxide, 34.1 of carbonic acid, and 10 of water.

The salts of manganese are decomposed by the alkalis, which throw down precipitates of a white colour, if the manganese is pure; the precipitate becomes speedily black from the action of the air, a property by which manganese is particularly distinguished. Prussiate of potash, and hydro-sulphuret of potash, throw down from them a white precipitate. They are not decomposed by the other metals,—a proof of the strong affinity of manganese to oxygen.

The fixed alkalis, in the dry way, exert a considerable action on oxidated manganese. When the black oxide is exposed to heat with twice its weight of dry soda or potash, a compound is formed of a dark green colour, which is soluble in water. During its solution, this substance exhibits rapid changes of colour; and hence has received the fanciful name of Mineral Chameleon. When a little of it is dropt into a large quantity of water, the solution is of a beautiful green colour, but in a few moments it changes to a purple, and then to a red. Or if upon a little of it a quantity of water is poured, the solution is of a deep green; but, in diluting it farther, it presents the same changes of colour. In a few hours it becomes colourless, a reddish precipitate being deposited: Or it is at once rendered colourless, without any precipitation, by a few drops of nitric or muriatic acid. These changes of colour have been supposed to be owing to successive but rapid changes in the degrees of oxidation, and may depend, in part, on the oxygen which water holds loosely dissolved. Or perhaps they may arise from the agency of water itself, producing hydrated oxides in the combination. Chevreul has supposed that there are two compounds, a green and a red, which by their intermixture form the other shades of colour. Chevillot and Edwards have shewn, that the compound can be obtained, by evaporation of the solution, in crystals of a red colour *. The compound to exhibit these phenomena, is best prepared by exposing to a red heat, in a covered crucible, one part of the black oxide with four parts of nitre; the acid of the nitre being decomposed, and serving, by the oxygen its decomposition affords, to keep the metal at the maximum of oxidation, in which state the alkali of the nitre combines with it.

Ammonia passed over oxide of manganese heated to redness, is decomposed; its hydrogen being attracted by the oxygen of the oxide, while its nitrogen combines with another portion of this oxygen, and forms nitric oxide.

Oxide of manganese combines with some of the earths, and with their vitrifiable compounds, and forms coloured glasses. The tinge it communicates is violet, and it is sometimes used in the formation of the pastes to imitate the gems. It communicates a similar colour to borax, phosphate of soda, and other vitrifiable salts; the colours being varied, according to the degree of oxidation. Bergman observed some striking results with regard to these by the

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* Annales de Chimie et Physique, tom. iv. p. 42. 287.

action of the blowpipe, which are very characteristic of this metal. If a little of the black oxide be mixed with the microcosmic salt, (phosphate of soda and ammonia), and brought into fusion on charcoal by the flame, a transparent vitreous globule of a violet red colour, or of nearly a ruby-red, if the quantity of oxide is considerable, is formed. If kept for some time within the interior blue flame, the colour disappears; but it is speedily restored by exposing the globule to the exterior yellow flame; and this may be repeated a number of times: or a little nitre added instantly restores the red colour. These effects evidently depend on the state of oxidation; the interior blue flame affording a sufficient quantity of inflammable matter to reduce the combination to that state of oxidation which gives the colour, while the exterior flame not affording this, operates merely by its temperature in favouring a higher degree of oxidation from the action of the air.

Manganese has not been combined with sulphur. Bergman could not effect their combination. Eight parts of oxide of manganese, he observes, by gentle heat in a retort, take up three of sulphur, and produce a yellowish-green mass, which is acted on by acids; the oxide being dissolved with effervescence, and with an odour of sulphuretted hydrogen. Vauquelin, however, affirms, that manganese and sulphur may be combined by fusion, forming a sulphuret, in which 100 of metal are combined with about 34 of sulphur *. Oxide of manganese unites with sulphuretted hydrogen; hence it is precipitated from its solutions by hydro-sulphuret of potash.

Pelletier combined phosphorus with manganese, by heating equal parts of phosphoric acid and manganese, with a little charcoal; or by projecting phosphorus on the metal, heated to ignition. The compound is of a white colour, has metallic lustre, is of a granular texture,

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* Annales d'Histoire Naturelle, vol. xvii. p. 16.

brittle, not altered on exposure to the air, but decomposed by heat: it is more fusible than the metal.

Manganese, from its great infusibility, is not easily combined with other metals; hence its alloys have been little examined. By exposing gold to a strong heat with black oxide of manganese, and a little oil, an alloy is formed of a pale yellow colour, with a shade of grey, of considerable lustre, very hard, and somewhat ductile: it is decomposed by heat, the manganese being oxidated. Manganese does not unite with silver or with quicksilver; with copper it forms an alloy which is ductile, and of a red colour. To iron it has a considerable affinity, and is very generally combined with it in nature; when combined artificially, the iron receives a white colour, and is rendered brittle. It does not unite, according to Gmelin, with lead. With tin, according to Bergman, it unites easily, but not with zinc, without much difficulty.

Manganese itself is not used, but its native black oxide is applied to several purposes. It is the substance from which oxygen can be most economically obtained; and from its power of affording oxygen, large quantities of it are consumed in the formation of the oxymuriatic acid employed in the art of bleaching. It has long been used in the art of glass-making; a small quantity of it being added to remove the green colour, which is derived from the oxide of iron usually contained in the materials from which glass is manufactured. The theory of its action was explained by Bergman. Iron in a low state of oxidation, gives to glass a green tinge, while, at a high degree of oxidation, it either does not enter into fusion, or it does not communicate colour. Manganese, in the state of black oxide, gives a violet colour, while, when in a lower state of oxidation, the glass is colourless. In adding, therefore, the black oxide to glass, when it yields oxygen to the iron, each metal passes to that state in which it does not communicate colour. To attain this, it is obvious that a certain proportion must be observed; for if there be an excess of the black oxide of manganese, it will produce a purple tint, while, if there be a deficiency of it, the green from the iron will prevail; and, from the difficulty of fixing the precise proportion, glass has generally a slight shade of one or other of these colours. In the art of glass-making, the black oxide of manganese is probably also useful by consuming the carbonaceous matter, and other substances present in the materials, susceptible of oxidation. In a large quantity, it is used in the composition of ornamental glass, to give a purple colour.

The native oxide of manganese is also used to give a black colour to earthen ware, a quantity of it being mixed with the composition before it is baked.

CHAP. XX.

MOLYBDENUM.

THE name of Molybdena was given to a mineral so similar in appearance, and in several of its qualities, to plumbago, that they had been considered as varieties of one substance. Scheele discovered that its chemical properties are entirely different from those of plumbago; and he farther discovered, that it contained sulphur, and that a peculiar metallic acid might be extracted from it. This has been reduced to the state of a metal, to which the name of Molybdenum is now appropriated. It has been examined by Pelletier, Hielm, Klaproth, Hatchet, and other chemists; and, more lately, minutely by Bucholz *.

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* Nicholson's Journal, vol. xx. p. 121.

There is only one ore of this metal, that in which it is mineralized by sulphur. It exists also in the state of an acid in an ore of lead. Different processes have been followed to extract it from the sulphuret. The most simple, and that which affords it nearly pure, is to treat it with nitric acid. On one part reduced to powder, five parts of diluted nitric acid are poured, and distilled to dryness; the distillation being repeated with new portions of the acid three or four times. The sulphur is converted into sulphuric acid, the molybdenum into molybdic acid or oxide; the latter, being sparingly soluble, remains, after washing, in the form of a powder. Another process, employed as well as the preceding one by Scheele, is to deflagrate the native sulphuret of molybdenum with four times its weight of nitre. Sulphate and molybdate of potash are formed. These are dissolved by warm water; any oxide of iron, in the native sulphuret, being left undissolved: by evaporation, the sulphate of potash and any undecomposed nitre crystallize: the compound of molybdic acid and potash remains uncrystallizable: it is diluted with water, and on adding sulphuric acid, the molybdic acid is precipitated, care being taken not to add an excess of acid, by which it might be re-dissolved. The acid still retains a little of the alkali combined with it, which, according to Scheele, may be separated by dissolving the precipitate in as small a quantity of water as possible, and boiling it for a few minutes with nitric acid *,—a method, however, which Bucholz found to succeed imperfectly. He farther found, that by calcination in the open fire, the sulphur of the native sulphuret is dissipated, and the metal brought to the state of an acid; and on this he founded a process, which had indeed been given before by Hielm †, more economical than either of Scheele's, and

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* Scheele's Chemical Essays, p. 227.

† Crell's Chemical Journal, vol. iii. p. 547.

affording the molybdenum more pure. The native sulphuret in powder is calcined in an open crucible with a strong fire, stirring it constantly, and diminishing the heat towards the end of the process, to prevent the fusion of the molybdic acid, and its combination with a little alumina and oxide of iron which the sulphuret contains. The residuum is digested repeatedly with liquid ammonia with which the molybdic acid combines, leaving the other substances undissolved. The solutions are mixed together and evaporated to dryness: the heat is raised to incandescence, by which the ammonia is expelled, and the molybdic acid remains, more or less reduced by the action of the ammonia favoured by heat *.

The reduction of molybdic acid to the metallic state, or rather the fusion of the metal into a globule, is extremely difficult. Scheele did not succeed in it; and Pelletier was equally unsuccessful; for although he reduced it by exposing its acid with charcoal and a little oil to the metallic state, it was so slightly agglutinated as to break under the fingers †. Hielm, although in many of his experiments he failed, in some others succeeded, when a very intense heat was excited by a powerful blast. The molybdic acid was reduced to a kind of slag, losing in this reduction about 25 *per cent.* of weight; and in some of the trials metallic globules were obtained ‡. Bucholz succeeded more completely, by urging molybdate of ammonia, or molybdic acid, surrounded with charcoal powder, with the most intense heat that could be raised by a forge-fire. After repeated experiments, a mass composed of scales agglutinated, and some small globules, both having metallic lustre, were obtained. And in repeating the experiment, he procured

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* Philosophical Magazine, vol. xvi. p. 202.

† Memoires de Chimie, tom. i. p. 213.

‡ Crell's Chemical Journal, vol. iii. p. 174. 180. 185. 339. 357.

pieces of one or two drachms, almost entirely fused, having a spherical surface, and metallic lustre *.

Molybdenum in its metallic state, according to Hielm, is of a yellowish grey colour, with metallic lustre: according to Bucholz, it is of a silvery white: it presents a granular fracture; is hard so as not to be easily broken; but does not appear to have ductility or malleability. Its specific gravity Hielm found to be 7000, and when its interstices were diminished, by more perfect fusion or compression, 7.400. Bucholz found it to be 8.611.

Molybdenum, though difficultly fusible, is easily oxidated. It is scorified on its surface by the external flame of the blowpipe. Bucholz, in exposing it to heat in a crucible, observed, that at a red heat it became of a brownish-yellow colour, which soon changed to violet, inclining to indigo. Pelletier remarked, that by calcination it is changed into a white oxide, and that it suffers a similar change by deflagration with nitre, the oxide remaining in combination with the alkali of the nitre. When fully oxidated, it becomes soluble in water, and acquires the properties of an acid.

Mr Hatchet, in his experiments on native molybdate of lead †, concluded, that this metal is susceptible of four degrees of oxidation: in the lowest it forms a black oxide; in the second, one of a blue colour; in a third, a green; and when saturated with oxygen, it forms the molybdic acid. These are best shewn in the de-oxidation of the acid. When subjected to the action of substances which partially abstract its oxygen, as, by immersing in its solution some of the metals, by transmitting through it a stream of hydrogen gas, or even by the action of light, it becomes blue. The green oxide appears to exist in some

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* Nicholson's Journal, vol. xx. p. 132.

† Philosophical Transactions, 1796, p. 336

of its salts, and is produced in the action of nitric acid on some of the solutions of molybdena, which it changes, first to a blue, then to a green, and at last to a yellow, of which last colour it precipitates the molybdic acid: the green may arise, therefore, from an intermixture merely of the yellow and blue. The black or brown oxide is obtained by the action of carbonaceous matter on molybdic acid at a high temperature: mixing it for example with charcoal powder, and submitting the mixture to a white heat; it remains in the state of a compact brown coloured mass. The degrees of oxidation which produce the blue oxide and the acid, are those which can be obtained with most certainty; in all of them the oxygen appears to be retained by a weak affinity. Bucholz, from the oxidation of the metal by heat, and by re-agents, concluded that the following oxides exist, the grey, brown, blue, bluish-green, yellow, and white, the last, indeed, being rather an acid. The existence of the grey is doubtful, and the green is probably a mixture of the blue and yellow. The existence of three oxides, therefore, appears to be established.

From the difficulty of procuring metallic molybdenum, the actions exerted on it by the acids are imperfectly known. Nitric acid acts on it rapidly, communicates oxygen, and converts it first into the blue oxide, and ultimately into molybdic acid. Hielm remarks, that by boiling in concentrated sulphuric acid it is dissolved, communicating to the acid a bluish-green colour, which, by longer boiling, nearly disappears, probably from the more perfect oxygenation of the metal, and its conversion into molybdic acid. Muriatic acid does not act on the metal, but oxymuriatic acid changes it into the blue oxide. The transitions from the state of the blue oxide to the acid, and of the acid to the oxide, take place from such slight changes of circumstances, that the proper salts of molybdenum, or those formed of the oxide and the different acids, are not easily obtained pure and insulated, and have not been examined. In general they are of a blue colour in solution, but can scarcely be crystallized without decomposition.

The brown oxide is of a copper colour, heavy, exhibiting an appearance of crystallization, insoluble in water, and apparently also insoluble in acids, their action converting it always into the blue oxide.

The blue oxide, according to Bucholz, is soluble in water, forming a solution of the same colour, which by evaporation becomes of a deep grey; and when cold, of a bluish-green. According to the same chemist, it reddens blue paper, and this even more powerfully than what has been named the Molybdic Acid; and it produces a brisk effervescence in acting on alkaline carbonates, forming with the alkali a blue solution. It may therefore be regarded rather as an acid than an oxide. It seems to be also in the state of a hydrate, or is a ternary compound of metal with oxygen and hydrogen, and to this its superior acidity may with probability be ascribed. From the experiments of Bucholz, it appears, abstracting its relation to water, to be composed of 100 of molybdenum, with 34 of oxygen.

What has been regarded as molybdic acid, is obtained by the processes already described, particularly by the agency of nitric acid, in the state of a yellowish-white powder; the specific gravity of which is 3.4. Its taste is sharp and metallic: it is soluble in water, requiring, according to Hatchet, 960 parts at 212° for its solution: the solution is of a pale-yellow colour, has little taste, but changes the infusion of litmus red. Exposed to heat, it is fused: the vitreous matter obtained by cooling, displays a crystalline structure: if heated strongly in an open crucible, it is volatilized, and the vapour, when condensed, forms a scaly powder of a yellow colour. It is decomposed by being heated with carbonaceous matter; and it is partially de-oxidated by a number of the metals, and by inflammable substances, being reduced generally to the state of the blue oxide: molybdenum itself produces this change, and this affords the best method of procuring the blue oxide. Paper, immersed in the solution, acquires a rich blue colour by exposure to the solar light. Bucholz concluded, from his experiments, that 100 parts of the metal absorb 48 of oxygen in passing to the state of acid; and therefore, that 100 parts of this acid consist of about 67 of metal, and 33 of oxygen.

This acid has relations to the other acids somewhat peculiar. Sulphuric acid dissolves it, with the assistance of heat, one ounce dissolving ten grains. The solution is colourless, but, as it cools, it becomes of a blue colour. Muriatic acid, digested on molybdic acid, with a strong heat, likewise dissolves it; the solution being of a pale yellowish-green colour: when saturated with potash, it becomes blue. Nitric acid has no effect on molybdic acid. Sulphuretted hydrogen partially de-oxidates it.

This acid combines with the alkalis: its salts named Molybdates, have been little examined. By combination with a portion of potash not sufficient to saturate it, it becomes more soluble in water: and its solution in boiling water affords, on cooling, small irregular crystals. The acid disengages carbonic acid from the alkalis. From Mr Hatchet's experiments, it appears, that, in entering into these combinations, a portion of the acid passes to the state of the oxide, a flocculent matter, convertible into molybdic acid by nitric acid, being deposited as the solution proceeds. No crystallizable compound could be obtained with the compound with potash. From that with soda, crystals of the form of four-sided tables were formed. From that with ammonia, a striated yellowish mass was obtained by evaporation, which dissolved again in water, without any residuum. From these salts, prussiate of potash does not throw down any precipitate; but if the alkali be super-saturated by an acid, it gives a reddish-brown precipitate. Muriate of tin added to their solutions, produces a white precipitate, which becomes blue when a little muriatic acid is added *.

Molybdic acid, in its action on the metals, is decomposed and reduced in part to the state of oxide. Scarcely any thing is known as to the results which might be obtained from presenting it to the metallic oxides. By adding solutions of the alkaline molybdates to the solutions of different metallic salts, the molybdic acid is precipitated, combined with the metallic oxide, and, by this method, several rich colours are obtained. That obtained from muriate of tin is a fine blue, and has been proposed to be fixed in cloth as a dye, the colour being very durable. The molybdates added to the vegetable dyes, add to the permanence of their colours †.

Molybdenum combines with sulphur, and produces a substance analogous to the native sulphuret. A similar compound is obtained by heating molybdic acid with sulphur, sulphurous acid being disengaged. The sulphuret, according to Bucholz, consists of 60 of metal, with 40 of sulphur. Pelletier found also, that it could be combined with phosphorus; the compound is not very different in appearance from the metal.

Molybdenum combines with a number of the other metals. A series of experiments was made by Hielm on the effects produced by the molybdic acid on metals at a high temperature, and also on the results obtained by exposing to the heat of a forge reguline molybdenum with the different metals. With platina, an alloy was formed of a close texture, of a light grey colour and metallic lustre, and fusible. With gold, the combination was less perfect. With silver, in equal parts, an alloy was formed of a granular texture, and brittle: with a larger proportion of silver, the compound was malleable, but not easily brought

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* Philosophical Transactions, 1796, p. 327.

† Philosophical Magazine, vol. xv. p. 15.

into perfect fusion. The amalgamation with quicksilver could not be effected. The alloy with copper, in equal proportions, was brittle, paler than copper, and not liable to tarnish. Of all the metals, iron he found to unite with molybdenum with most facility, and in greatest quantity; the alloy, from equal quantities, was of a bluish-grey colour, brittle, having a granulated texture, and not easily fused into a perfect button. Lead combines with about one-tenth, acquires greater hardness and a whiter colour. With tin, in various proportions, alloys are formed, brittle, soft, and of a dark-grey colour. With zinc, a black spongy mass is formed, not easily fused into a metallic button. Nickel and molybdenum, fused in equal quantities, form an alloy of a light grey colour, granulated, hard, and brittle. Cobalt melts with it, and forms a brittle alloy of a bluish grey colour. The alloy with manganese is not easily melted into a metallic globule. Bismuth, by an alloy of molybdenum, acquires a closer texture, and a black colour: the alloy is also very brittle. With arsenic a black spongy mass is formed. None of these alloys seem to be applicable to any useful purpose *.

CHAP. XXI.

TUNGSTEN.

Under the name of Tungsten, a substance was known to mineralogists, which Scheele discovered to contain a peculiar metal, existing in it, as he supposed, in the state of an acid united with lime. The same metallic matter was afterwards discovered by Messrs. D'Elhuyart, Spanish

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* Crell's Chemical Journal, vol. iii. p. 552.

chemists, united with iron and manganese in another mineral, named Wolfram. These are therefore the ores of one metal, to which the name of Tungsten has been appropriated.

From the first of these ores the tungstic oxide or acid is extracted by digesting the ore, reduced to a fine powder, in three parts of nitric acid ; a yellow powder remains, which, after having been washed with water, is digested with ammonia, by which a portion of it is dissolved. These alternate operations are repeated : the ammoniacal liquors consist of the tungstic oxide, combined with ammonia : it is precipitated by adding nitric acid to saturate the alkali, is again washed with water, and exposed to a moderate heat, to drive off any ammonia that may remain combined with it. From wolfram the oxide of tungsten may be obtained, according to the method of D'Elhuyart, by digesting it with muriatic acid, which dissolves the iron and manganese : the yellow powder which remains, is treated with ammonia, as in the preceding process : to the ammoniacal solution nitric acid is added to saturate the alkali : the oxide of tungsten is precipitated, or is obtained in still larger quantity by evaporating the whole to a dry mass, and calcining this under a muffle, by which the nitrate of ammonia is dissipated. Potash has sometimes been employed to abstract the acid in these processes; but this is improper, a portion of the potash and of the acid remaining combined with the oxide of tungsten, as Bucholz has shewn *; and when it is digested in ammonia, a portion of it also unites with the others, forming a quaternary compound, from which the pure oxide cannot afterwards be obtained by heat, and which is extremely difficult of reduction.

The oxide of tungsten was reduced by Messrs. D'Elhuyart to the metallic state, by exposing it, moistened with

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* Annals of Philosophy, vol. vi. p. 198.

oil, in a crucible lined with charcoal, to an intense heat. After two hours a piece of metal, weighing 40 grains, slightly agglutinated, was found at the bottom of the crucible. Klaproth and other chemists have been unable to effect this reduction, or at least to fuse the metal completely. Yet it has been obtained in a more or less perfectly agglutinated state, usually in a kind of metallic sand. Ruprecht, by a process similar to the preceding one, procured it in small metallic globules *: and it has been obtained by Guyton in a well fused mass †; and also by Messrs. Aikin and Allen ‡. Mr Children fused it in the intense heat of his galvanic battery.

Tungsten, in its metallic state, is described by the Spanish chemists as of a greyish-white colour, with considerable brilliancy, brittle, and very hard. They state its specific gravity so high as 17.6, so that in this property this metal would stand next to gold: this appears to be confirmed by the experiments of Aikin and Allen, from which its specific gravity is stated at 17.22. Ruprecht had stated it no higher than 6.823; and Guyton, even when it had been perfectly fused, at 8.3406; but the first result has been confirmed by Bucholz, the specific gravity he obtained being 17.4, estimated from the metal in small grains which he obtained.

The great infusibility of tungsten is apparent from the preceding account of the processes employed to obtain it. It appears to be very susceptible of oxidation, as its surface tarnishes when heated in contact with the air, and a quantity of oxide is formed.

Scheele supposed that the white powder, which is obtained by digesting muriatic or nitric acid on tungsten, adding ammonia to the residuum, and then neutralizing

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* Crell's Chemical Journal, vol. iii. p. 301.

† Nicholson's Journal, 4to, vol. iv. p. 191.

‡ Philosophical Magazine, vol. xii. p. 407.

this ammoniacal liquor with nitric acid, is the acid of tungsten. Its acid powers are indeed undoubted: it is very soluble in water, requiring not more than 20 parts at 212° for its solution: its taste is sour, and it reddens the infusion of litmus: it also neutralizes the properties of the alkalis, and forms with them crystallizable salts *. But, according to the Spanish chemists, this substance is a triple compound of oxide of tungsten, and of the acid and alkali employed in the process; nor does there appear to be such a substance as tungstic acid, the product of the highest degree of oxidation being only the yellow oxide. This has been confirmed by Vauquelin and Hecht †. The white powder, considered by Scheele to be acid of tungsten, they found, by analysis, to be a triple salt; and it is only the yellow powder, obtained by boiling this in a concentrated acid, that is pure. It has no acid property; is quite insoluble in water; tasteless, and produces no change in the vegetable colours; and although it is capable of combining with the alkalis, this is common to it with many metallic oxides. It is obtained pure by boiling an acid on the white powder obtained by the process of Scheele, and exposing the yellow powder, which is thus precipitated, to a red heat; or by digesting wolfram in nitric acid, dissolving the yellow powder that remains in ammonia, evaporating this ammoniacal solution to dryness, and expelling the ammonia from the dry mass by raising the heat: the residuum is the yellow oxide of tungsten. By a strong heat it is partially de-oxidated, and assumes a green colour: when fused with borax, or phosphate of ammonia, it gives a blue tinge, and a rich blue colour is produced when iron, zinc, or tin, is immersed in the solution of its triple salts, and a few drops of muriatic acid added. It does not change its colour by exposure to light.

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* Scheele's Essays, p. 289.

† Journal des Mines, No. xix. p. 19.

Bucholz had observed the production of a brown oxide, from the partial reduction of the ammoniacal oxide by heat. Berzelius obtained it by passing a current of hydrogen gas over the yellow oxide, heated to ignition in a tube. It is of a flea-brown colour, very inflammable, so as to take fire at a temperature considerably under a red heat, and thus passing into the yellow oxide; and neither soluble in acids or alkalis. It consists, according to his analysis, of 85.84 of tungsten, with 14.16 of oxygen, or 100 with 16.5 *. The yellow oxide had been inferred by Messrs. D'Elhuyarts to be composed of 80 of metal with 20 of oxygen, or 100 with 25; and the same proportions are assigned by Berzelius, from his analysis of tungstate of ammonia and tungstate of lead.

Tungsten was found by Messrs. D'Elhuyart insoluble in sulphuric, nitric, or muriatic acid. Ruprecht found, that even nitro-muriatic acid boiled on it, did not dissolve any sensible quantity. Nor is its oxide much more soluble in the acids, as is apparent from the processes by which it is extracted from its ores; and Vauquelin found, that even by boiling it with the acids, scarcely any sensible quantity was dissolved. It combines with more facility with the alkalis, at least when a portion of acid is present, and forms soluble ternary compounds.

It does not form any direct combination with sulphur; but Berzelius effected the combination, by heating yellow oxide of tungsten with sulphuret of mercury, covered with charcoal. The sulphuret he found to be of a greyish black colour, with metallic lustre when rubbed; and composed of 75 of tungsten, with 25 of sulphur.

The Spanish chemists sought to discover the results of its combinations with the other metals, by exposing these metals and the oxide of tungsten to a strong heat. Gmelin made a series of similar experiments, and, by adding to

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* Annals of Philosophy, vol. iii. p. 246.

the mixture a little charcoal powder, rendered the reduction of the oxide more certain. They present, however, no interesting results; and, indeed, in almost all of them, from the extreme infusibility of tungsten, the combinations were difficult and imperfect; and the uncertainty of the metal having been obtained pure, render such researches of little value.

Guyton has found that the oxide of tungsten gives great permanence to the vegetable colours.

CHAP. XXII.

CHROME.

This metal was discovered by Vauquelin. It exists in the state of an acid, combined with oxide of lead, in what was named Red Lead Ore, found in Siberia. Vauquelin found that this consists of a peculiar metallic acid united with oxide of lead, and he reduced this acid to the metallic state. His researches were confirmed by those of Klaproth and Gmelin. Chrome derives its name from the brilliant colours which it presents in its saline combinations. It has since been discovered in various minerals, particularly combined with iron, and also in some of the gems, as the emerald and ruby, of which it is probably the colouring matter. It has also been found as an ingredient in some of the meteoric stones.

Vauquelin extracted the metal, by adding to the ore muriatic acid, which combines with the oxide of lead, and forms a compound that is precipitated, the chromic acid remaining in solution. To abstract a little muriatic acid combined with it, oxide of silver is cautiously added, and the pure chromic acid being decanted from the precipitate of muriate of silver, and evaporated, is exposed to a very strong heat excited by a forge, in a crucible of charcoal, placed within another of porcelain. It is thus reduced to the metallic state. Chromate of Iron being a more abundant mineral, chrome is now generally extracted from it. The process given by Vauquelin is complicated, but its essential steps are to calcine the chromate of iron with half its weight of nitre; the mass is lixiviated, and the chrome being converted by the oxygen of the nitre into an acid which combines with the potash, the liquor holds chromate of potash dissolved. Any excess of alkali is removed by adding nitric acid, and the salt is crystallized. It is redissolved, and nitrate of mercury at the minimum of oxidation is added; chromate of mercury is precipitated; this is washed with water, the mercury is expelled by heat, and oxide of chrome remains, which may be reduced. It is to the researches of this chemist in his first memoir *, and in a subsequent one †, that we are indebted principally for a knowledge of the properties of this metal.

Chrome is of a white colour, inclining to grey: it is very brittle: its fracture presents a radiated appearance, needles crossing in different directions; its specific gravity is 5.9.

It is difficult of fusion. Before the flame of the blowpipe, it does not melt. When fused by having been exposed to the heat necessary to its reduction, it presents crystalline filaments, rising above the metallic mass.

It is oxidated by the action of atmospheric air at a high temperature. When heated by the blowpipe, its surface tarnishes, and is at length covered with a light green crust, which is an oxide. By a farther oxygenation, by treating it repeatedly with nitric acid, it is brought to the

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* Nicholson's Journal, 4to, vol. ii. p. 587.

† Philosophical Magazine, vol. xxxv. p. 20.

state of an acid, the colour of which is red. Vauquelin supposed that another oxide besides the green exists, for the green oxide, long heated, changes its colour to yellow. And he afterwards discovered an oxide intermediate between the green oxide and the acid, and obtained from the decomposition of the nitrate by heat. Berzelius could not obtain any oxide at a lower degree of oxidation than the green, but he confirmed the discovery of the intermediate oxide from the decomposition of the nitrate. It is of a deep brown colour, rather brilliant; it is insoluble in alkalis and in acids, but muriatic acid decomposes it, forming oxymuriatic acid gas. Vauquelin had inferred, that the chromic acid is composed of 60 of metal and 40 of oxygen. Berzelius has inferred, from experiment, that the green oxide is composed of 70.24 of chrome, and 29.76 of oxygen, or 100 with 42.37; and the acid of 54.13 of chrome, and 45.87 of oxygen, or 100 with 84.74.

Chrome is not easily acted on by the acids. Even when reduced to a fine powder, and treated with concentrated boiling nitric acid, it is oxidated with much difficulty, and communicates to the acid only a green tinge. Nor is any sensible quantity of it dissolved, until it has been treated repeatedly with considerable quantities of the acid. Even oxide of chrome is with difficulty acted on by the acids, and the salts of chrome are not much known. The sulphate is easily decomposed by heat, and is rendered insoluble; the muriate by evaporation gives a red powder, which attracts humidity from the air, and forms a solution of a rich green colour. The solution of the phosphate is of a fine emerald green; that of the oxalate has an amethystine hue. Oxide of chrome is soluble in the alkalis; the solution is of a green colour, and is decomposed by boiling, the oxide being precipitated.

Chrome, in the state of acid, appears to be more susceptible of combination; and this acid being obtained from its native combinations, its chemical relations have been more examined. To obtain it perfectly pure, the process given by Vauquelin is, to form chromate of barytes by adding nitrate of barytes to a solution of chromate of potash; the chromate of barytes is dissolved in dilute nitric acid, and is decomposed by adding sulphuric acid; the solution containing the chromic acid, being filtered, is evaporated to dryness, so as to expel the nitric acid.

Chromic acid is very soluble in water: the taste of the solution is sharp and metallic: it is of an orange-red colour: by evaporation, spontaneous or with a gentle heat, it affords crystals, in slender prisms, of a ruby-red colour. These are deliquescent.

Chromic acid is easily reduced to the state of the green oxide. Heated by the blowpipe on charcoal, it leaves a green infusible matter. Melted with borax, or phosphoric acid, it gives to the globule an emerald-green colour. Paper wetted with it, and exposed to the solar light, assumes a green colour; and the same colour, which is the indication of its partial de-oxidation, is produced by immersing most of the metals in its solution; or by boiling the solution with ether or alkohol. It dissolves in alkohol in the cold, but the solution soon becomes green, from the decomposition of the acid. Muriatic acid heated with it, produces oxymuriatic gas, and the fluid assumes a beautiful deep green colour. The solution of chromic acid gives a greenish brown flocculent precipitate with hydro-sulphuret of potash, and one of a yellowish brown colour with tannin.

This acid combines with the alkalis, earths, and metallic oxides, forming neutral salts named Chromates. To the observations of Vauquelin on these salts, some facts have been added by Professor John *. The alkaline chromates are soluble; the colour of their solutions is an orange-yellow, and, by evaporation, they afford crystals of the same

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* Annals of Philosophy, vol. iv. p. 424.

colour: they afford oxgen gas by heat, and the residuum of this operation has a green colour. They are decomposed by the mineral acids, and several of the earths, and by double affinity, by the greater number of earthy and metallic salts. The chromate of potash crystallizes in rhomboidal prisms, which when neutral are of a citron-yellow colour; when they have an excess of acid, the colour is orange-red; the chromate of soda, according to John, is in six-sided tables, transparent, of a dark yellow colour; that of ammonia is in plates of great brilliancy on the surface, of a rich yellow colour. It appears from the observations of Godon*, that the alkalis, by their affinity to this acid, enable the oxide to attract oxygen from the air, and be acidified, when it is exposed with the alkali to a high temperature.

The earthy chromates resemble the alkaline chromates in their general properties. Chromate of barytes is of very sparing solubility: it consists, according to Vauquelin, of 62.2 of base, and 37.4 of acid: according to Berzelius, of 59.85 of base, and 40.15 of acid. Chromate of strontites is also insoluble, and forms by precipitation a yellow powder. Chromate of lime is very soluble; its solution affords by evaporation silky flakes of a yellowish brown colour. Chromate of magnesia is also a very soluble salt; it crystallizes in prisms, transparent, and of a fine topaz-yellow colour. Chromate of glucine is soluble, and not crystallizable: that of ittria is soluble, and by evaporation forms dendritic crystals. The acid unites, according to Godon, with silex, when this earth is in a state of extreme division, and forms a matter of a rose colour, insoluble in water, which is not changed by heat.

The combinations of this acid with metallic oxides are in general possessed of very beautiful colours, and are well adapted to form the finest paints. That with oxide of lead

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* Annales de Chimie, tom. liii. p. 224.

has an orange-yellow, of various shades, according to the excess of acid or of oxide; the proper chromate of lead consists, according to Berzelius, of 68.24 of oxide, and 31.76 of acid: that with mercury is of a vermilion red; with silver, a carmine red if there is a slight excess of acid, otherwise reddish brown; with zinc and bismuth, the colours are yellow; with copper, cobalt, and antimony, they are brown and dull.

The combinations of this metal with the simple inflammables, or with the other metals, have not been examined.

Chrome furnishes in its combinations the most beautiful and durable pigments; and as it has now been found in considerable quantity in nature, it is employed in the formation of these; the chromates of lead are highly valued in miniature painting, for their beauty, and for not being liable to alteration. The oxide is used in porcelain painting, forming a beautiful green; it also forms enamels of a rich colour, green and yellow, and it might be employed in forming ornamental glass to imitate the gems.

CHAP. XXIII.

TELLURIUM.

The existence of this metal was suspected by Muller, in an ore of gold found in some of the mines in Transylvania. He even made experiments on the metal which is combined with the gold in this ore, and Kirwan gave it a place in his mineralogy, under the name of Sylvanite, on the authority of Muller's experiments *. The discovery

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* System of Mineralogy, vol. ii. p. 324.

was afterwards confirmed by Klaproth, who denominated this metal Tellurium, and to him we are principally indebted for the knowledge of its properties. In several of its qualities, it has a close resemblance to antimony, but in others it differs entirely from that metal. It occurs in several ores, principally alloyed with small portions of gold, silver, iron, lead, and copper.

Pure tellurium, obtained from any of its native combinations, is of a tin-white colour, verging into lead-grey, with metallic lustre: its fracture is foliated: it is very brittle, so as to be easily reduced to powder. It is one of the lightest metals; its specific gravity being 6.115.

Tellurium is easily fused: it melts before ignition, at a heat somewhat higher than that which melts lead. It is also capable of being volatilized, and, according to Gmelin, is as volatile as arsenic. When cooled without agitation, its surface presents a crystallized appearance.

When heated before the blowpipe on charcoal, it inflames, giving a vivid light, blue, and greenish on the edges: it is dissipated in greyish-white vapours, having a pungent odour, which, condensed, form a white oxide. If this oxide is heated on charcoal, it is reduced with a kind of explosion, but is again speedily converted into vapour, and oxidated by continuing the heat. If heated in a glass retort it fuses: and, when solid, has a straw-yellow colour and striated texture. The oxide, precipitated from some of its metallic combinations, appears from Klaproth's experiments, to contain about 20 parts of oxygen combined with 100 of the metal: according to those of Berzelius, 100 are combined with 24.4, or 24.8 *. It is reduced by being exposed to heat with oil, or any carbonaceous matter.

Tellurium is oxidated and dissolved easily by the acids. Sulphuric acid poured on it, gradually acquires, even in

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* Annals of Philosophy, vol. iii. p. 250.

the cold, a deep purple colour: on adding water, this colour disappears, and the small quantity of metal dissolved separates in black flocculi. Heat destroys the colour, and a white precipitate is thrown down.

With nitric acid, it yields a colourless solution, which is not rendered turbid by water. The concentrated solution gives slender needle-shaped crystals, aggregated so as to form a dendritic appearance.

Muriatic acid, to which a little nitric acid has been added, affords a similar transparent solution: this solution is decomposed by water, and a white precipitate is thrown down, which, Klaproth remarks, is not a pure oxide, but a sub-muriate; by repeated affusions of water, it is almost entirely dissolved. It is also thrown down by alkohol. Sulphuric acid, diluted with two or three parts of water, to which a little nitric acid has been added, dissolves also a large portion of the metal, and the solution is not decomposed by water. Tellurium burns in oxymuriatic gas: the product is fusible, volatile, and capable of crystallizing, in condensing from the state of vapour.

The alkalis throw down from the saline solutions of tellurium, precipitates of a white colour, which retain a portion of the alkali, and are soluble in acids. If an excess of alkali be added, the precipitate is entirely re-dissolved, as it is also by the alkaline carbonates. The pure oxide is also dissolved by the fixed alkalis, and even by ammonia by digestion.

The solutions of tellurium are not precipitated, nor rendered turbid by prussiate of potash, a property which it has in common with gold, platina, and antimony. Tincture of galls produces a flocculent yellow precipitate.

They are decomposed by several of the metals, which attract the oxygen combined with the tellurium, and precipitate it in its metallic state. This is done by zinc, iron, tin, and antimony. Phosphorus put into the muriatic solution, is gradually coated with metallic laminæ.

Tellurium has a peculiar relation to hydrogen. Ritter observed the singular fact, that when it is employed as the conducting wire in the experiment of galvanic decomposition of water, oxygen gas is given off at the positive side; but at the negative side, a brown powder falls down. This he supposed to be a compound of hydrogen and tellurium, the only known compound, at the time he drew this conclusion, of a metal with hydrogen in the solid state *. Davy repeated this experiment; at the negative side he observed a purple fluid to separate and diffuse itself through the water, which became at length turbid, and deposited a brown powder. The purple fluid he found to be a solution of a compound of tellurium and hydrogen in water; in being diffused, it is acted on by the oxygen of the air dissolved in water, loses part of its hydrogen, and forms the solid hydruret, which is precipitated. When uncombined it is gaseous; and if sulphuric or muriatic acid be present in the water, it is not dissolved, but is disengaged, and may be collected. This aeriform compound of tellurium and hydrogen, has a smell similar to that of sulphuretted hydrogen. It is soluble in water, forming a solution of a claret colour, which becomes brown, and deposites tellurium on exposure to the air. It combines with the alkalis. And it precipitates the greater number of metallic solutions. The direct combination of tellurium with hydrogen, appears to be produced by heating the metal in hydrogen gas †. Berzelius has inferred, though not from results perfectly determined, that telluretted hydrogen is composed of 100 of tellurium, with 3.1 of hydrogen ‡.

In employing tellurium as the negative galvanic surface in the action of a powerful battery on potash, Ritter observed that potassium is not obtained. Davy found, that

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* Nicholson's Journal, vol. xxiv. p. 518.

† Philosophical Transactions, 1810.

‡ Nicholson's Journal, vol. xxxvi. p. 154.

in this case the tellurium combines with the hydrogen of the water of the potash, and this combines with the potash, forming a compound soluble in water. An alloy of tellurium and potassium appeared also to be produced, and these two substances, when heated gently, combine with energy, producing vivid light and heat, and forming a compound of a dark colour, brittle, with a crystalline fracture. The same alloy is produced by heating potash and oxide of tellurium with charcoal: and when this alloy is acted on by diluted sulphuric acid, the hydrogen evolved, holds tellurium dissolved.

When fused in a gentle heat, with an equal quantity of sulphur, tellurium forms a lead coloured striated substance. If this be heated to ignition in a retort, part of the sulphur is sublimed, elevating a little tellurium with it. The alkaline sulphurets precipitate it from its solutions, the precipitate being of a brown or black hue, and being composed either of the metal or its oxide in combination with sulphur. On burning charcoal, it burns with a pale blue flame, and a white smoke, as the compound of the metal and sulphur formed by direct union does.

The alloys tellurium forms with the metals have scarcely been examined. It does not easily amalgamate with quicksilver, even when their action is aided by heat *.

The other chemical relations of this metal have not been discovered, nor, from the small quantity of it which can be obtained, has it been applied to any use.

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* Klaproth's Analytical Essays, vol. ii. p. 1. &c.

CHAP. XXIV.

TITANIUM.

THE metal to which this name is given, exists more abundantly in nature than some of the other newly discovered metals. Mr Gregor first discovered, in a kind of ferruginous sand found in the vale of Menachan in Cornwall, what appeared to him to be the oxide of a new metal, which he attempted in vain, however, to reduce *. Klaproth, some years afterwards, in submitting to analysis a fossil known by the name of Red Schorl, discovered it to be the oxide of a metal until then unobserved, to which he gave the name of Titanium †. Analysing afterwards the mechanite of Cornwall, he recognized in it the same oxide ‡: and it has since been discovered in other minerals. To extract it, the method usually employed has been to fuse the red schorl or titanite with potash; on adding water, the potash is dissolved, holding a portion of the oxide dissolved, but the greater part remains undissolved, in combination, as Vauquelin shewed, with a portion of potash, and forming a compound, which is soluble in acids. On being dissolved in muriatic acid, and the solution heated, the oxide is deposited. It is in such a state of aggregation, however, that it is difficult to collect it. Laugier has found, that the easiest method of insulating it, and obtaining it pure, is to add to the muriatic solution, oxalate of ammonia; a white flocculent precipitate is immediately

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* Journal de Physique, 1791.

† Analytic Essays, vol. i. p. 200.

‡ Ibid. p. 499.

thrown down; the iron, which almost always accompanies titanium, remains in solution; the precipitate consists of oxalate of titanium, with a little muriate of ammonia: by calcination it affords pure oxide of titanium, of a yellow colour, which becomes white when cold *.

The reduction of oxide of titanium is extremely difficult. Vauquelin and Hecht obtained only an imperfectly agglutinated mass, in which were minute metallic globules †. This mass, and the globules it contained, were of a yellowish red colour, with shades of purple, and other hues. Lampadius appears to have obtained it in more perfect fusion. Its colour was a copper red, with much metallic brilliancy, but liable to tarnish from exposure to the air: it was brittle ‡. Laugier, in reducing the pure oxide, obtained in the middle of the mass layers mamillary on the surface, of a golden yellow colour, which he regarded as metallic titanium. From the experiments of Vauquelin, it appears to be volatilized in intense heats.

It is probably susceptible of oxidation without much difficulty, as the metallic mass in which it is obtained changes its colour when heated in contact with the air, assuming tints of purple and blue. In the native red oxide, the metal appears to be in a higher state of oxidation, and it can be oxidated still more highly by fusing it with potash. On dissolving the fused matter, a white substance precipitates, which, according to Vauquelin and Hecht, is an oxide containing 0.11 of oxygen: but it is uncertain but that it contains a portion of potash.

Titanium is not much acted on by the acids. Laugier found the yellow matter he obtained to be scarcely acted on by nitric acid. The native red oxide Kla-

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* Annales de Chimie, tom. lxxxix. p. 306.

† Journal des Mines, No. xv. p. 10.

‡ Nicholson's Journal, vol. vi. p. 62.

proth found to be insoluble in sulphuric, nitric, muriatic, and nitro-muriatic acids. But when it is fused with twice its weight of potash, it appears, from the experiments of Vauquelin, to absorb more oxygen, and to combine with carbonic acid; and the oxide, in this compound, is soluble in acids, the carbonic acid being disengaged with effervescence.

Sulphuric acid, boiled on titanium, oxidates and dissolves a small portion of it. When added to the carbonate obtained by the process just described, it disengages the carbonic acid, and forms a solution, which, on evaporation, becomes gelatinous. Nitric acid has scarcely any action on the metal or on the red oxide; but, when boiled on the carbonate, it dissolves its oxide, and the solution, by spontaneous evaporation, affords rhomboidal crystals; by boiling, it becomes turbid. Muriatic acid acts on metallic titanium, and dissolves it: it combines also with the oxide of the artificial carbonate: the solution, when heated, becomes gelatinous, or flocculent, and transparent crystals form in it when cooled: when boiled, oxymuriatic gas is formed, and a quantity of white oxide is separated from the combination. Phosphoric and arsénic acids were observed by Klaproth to separate oxide of titanium from the other acids, producing compounds which are insoluble, and which are thrown down as white precipitates. Chenevix observed, that these are re-dissolved by muriatic, but not by any other acid.

The salts of titanium give white precipitates on the addition of the three alkalis or alkaline carbonates. Prussiate of potash produces a green precipitate, but this colour, Lowitz and Vauquelin found to be owing to the presence of iron; the colour with pure titanium being a brownish yellow or red: tincture of galls gives a brownish-red. The metals produce a partial de-oxidation, which gives rise to various changes of colour: zinc changes the colour from a yellow to a violet, which passes to indigo: tin produces first a pale red tint, which deepens to bright purple red.

The fixed alkalis, fused with red oxide of titanium, cause it to pass to a higher degree of oxidation. When melted with borax, it forms a glass of hyacinthine colour.

Titanium does not appear to combine with sulphur. Its solutions are not decomposed by sulphuretted hydrogen; hydro-sulphuret of potash throws down from them a precipitate of a brownish-red colour. Mr Chenevix combined it with phosphorus, by exposing to a very violent heat phosphate of titanium, mixed with charcoal and borax, in a double crucible luted. The phosphuret was of a pale white colour, with some lustre, brittle, of a granular texture, and not very fusible.

The combinations of titanium with the other metals are scarcely known. In the experiments of Vauquelin and Hecht, in which they exposed to heat several metallic oxides with oxide of titanium, and a little oil and charcoal, no perfect combination appears to have been established, except with iron. This alloy was of a grey colour, with metallic particles, brilliant, and of a golden colour intermixed.

Oxide of titanium was used, previous to the discovery of its nature, to give a brown or yellow colour in painting on porcelain; but it was found difficult to obtain a uniform shade, probably from the intermixture of oxide of iron in the native oxide. The pure oxide, obtained by an artificial process, might be used with advantage.

CHAP. XXV.

URANIUM.

The discovery of this metal is due to Klaproth. A mineral had been known by the name of Pechblende, respecting which different conjectures had been formed: he shewed, that it contains a new metal, to which he gave the name of Uranium, combined with sulphur. He afterwards discovered the same metal in other minerals, in the state of oxide, in what had been named Green Mica, and in another, which has received the name of Uranitic Ochre. It is from his experiments principally that our knowledge of its properties are derived *. It is extracted from the sulphuret by digesting with nitric acid; precipitating the solution by ammonia; re-dissolving the precipitate in nitric acid, and evaporating to crystallization. The green coloured crystals that are thus obtained are nitrate of uranium; by exposure to a red heat the nitric acid is expelled or decomposed, and the yellow oxide of uranium remains. Klaproth found its reduction extremely difficult. By forming it into a paste with oil or wax, and exposing it in a charcoal crucible to the intense heat of a porcelain furnace, estimated at 170° of Wedgwood, he obtained in one experiment only an aggregate of metallic grains; in another a metallic button. The latter was of a dark grey colour, with metallic lustre, hard, of a fine grain in the fracture, and had considerable cohesion. Its specific gravity was 8.1.

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* Analytic Essays, vol. i. p. 476.

This metal is even more infusible than manganese, as a perfect reduction of oxide of manganese to the reguline state was obtained in a heat, in which uranium, though reduced, was imperfectly agglutinated. Mr Children did not succeed either in fusing or reducing the oxide of uranium, in the intense heat of his large galvanic battery.

Uranium does not appear to be very susceptible of oxidation, as, when small portions of the metal were exposed on charcoal to the flame of the blowpipe, it suffered no change. According to Bucholz, however, when it is heated to redness it inflames, and forms an oxide of a greyish colour. A more perfect oxide is obtained by causing nitric or nitro-muriatic acid to act on the ores of the metal, and precipitating it by the addition of an alkali. It is of a yellow colour; is insoluble in water: when raised to ignition, it acquires a brownish grey colour. According to Vauquelin, another oxide exists of a green colour. It is obtained by decomposing the solution of the muriate by an alkali. It appears to be converted into the yellow oxide by the action of nitric acid, aided by heat. This yellow oxide does not form with the acids perfectly neutral salts, nor do its salts crystallize. The green oxide forms with the acids crystallizable salts of a yellowish green colour: the former oxide is soluble in the alkaline carbonates, the latter is not *. According to Bucholz, the protoxide is composed of 100 of metal, with 8.3 of oxygen; the peroxide of 100 with 25.

The action of the acids on the metal has not been examined. Klaproth only observed that nitric acid is decomposed by it, and the metal is dissolved. He made several experiments, however, on the saline combinations formed by the action of the acids on the native oxide.

By diluted sulphuric acid, assisted by a gentle heat, it is soon dissolved; the solution by evaporation affording

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* Nicholson's Journal, vol. xxv. p. 69.

prismatic crystals of a lemon-yellow colour. Nitric acid diluted, dissolves it also; the solution affording crystals in hexagonal tables of a light green colour, and transparent, but liable to alteration from exposure to the air. The solution in muriatic acid affords, by evaporation and rest, crystals in rhomboidal tables of a yellowish green colour. Phosphoric acid dissolves the oxide, and the solution, after some time, deposites pale yellow flocculi, which are the phosphate, sparingly soluble in water.

The alkalis throw down the oxide from the solutions of these salts, of a lemon-yellow colour; with the alkaline carbonates, the precipitate inclines more to white, and is re-dissolved on an excess of the carbonate being added. The pure alkalis do not re-dissolve the oxide, but they change its colour to a brown. Prussiate of potash throws down a deep brown-red precipitate; sulphuret of ammonia, one of a brownish yellow colour; tincture of galls, a small quantity of a blackish precipitate, which, on the farther addition of an alkali, is copious, and of a chocolate brown. The neutral oxalates cause no precipitation. The solutions are not altered by the metals, not even by iron or zinc, which proves the strong attraction exerted by uranium to oxygen.

On mixing the yellow oxide with twice its weight of sulphur, and exposing it to heat in a retort, Klaproth found the greater part of the sulphur to be volatilized, but a portion remained combined, forming a compact mass of a deep brown colour, from which, by again exposing it to heat, the greater part of the sulphur was expelled.

No experiments have been made on the combinations of uranium with the other metals. Its oxide appears, from Klaproth's experiments, to combine with vitrifiable substances, and gives to them a brown or green colour. Heated with phosphate of soda before the interior flame of the blowpipe, it forms a transparent globule of a grass-green colour, which becomes yellow on the addition of nitre, Fused on porcelain by the usual flux in the enamelling furnace, he found it to give an orange-yellow colour.

CHAP. XXVI.

TANTALUM.

The metal to which this name has been given, was discovered by Ekeberg, a Swedish chemist, in two minerals found in Sweden, which he named Tantalite and Yttrotantalite. In the first it exists with manganese and iron; in the second with iron, and a combination of the new earth ittria. The oxide of tantalum is extracted from these minerals by fusion with potash, with which it combines, forming a compound soluble in water, and from which the oxide is precipitated by an acid. It is obtained in the form of a white powder, the specific gravity of which Ekeberg found to be 6.500. When this is exposed to a strong heat with powder of charcoal, it is reduced to a hard globule, having metallic lustre at its surface, but a dull fracture, of a greyish black colour. The acids have no other effect on this metallic matter, than to bring it to the state of white oxide: in whatever quantity they may be added, they do not dissolve it. This oxide, or that which is obtained by the action of an alkali, does not change its colour in a red heat. It melts before the blowpipe with borax, or phosphate of soda, but gives no colour to either of them. The fixed alkalis dissolve it, but it is insoluble in any acid. From these characters, Ekeberg considered this as a metallic substance, different from any before known. It has a resemblance, in some of its properties, to the oxides of tin, tungsten, and titanium, all of which are soluble in the alkalis, and insoluble in acids. But oxide of tin may be rendered soluble, and is easily reduced: oxide of tungsten is soluble in ammonia, it is rendered yellow by acids, and it communicates colours to borax and phosphate of soda: and oxide of titanium is soluble in the acids after it has been acted on by alkalis, and communicates a yellow colour to borax *.

Mr Hatchet, in examining some minerals in the British Museum, observed one similar in appearance to chromate of iron, which, on submitting to analysis, he found to be composed of oxide of iron, with a peculiar metallic oxide or acid. This latter substance he found to differ from all known metallic bodies; and to the metal considered as its base, he gave the name of COLUMBIUM, as the produce of America.

On the discovery of tantalum by Ekeberg, there appeared to be a considerable resemblance between its oxide and the oxide of columbium. The latter, extracted from its ore by exposing it to heat with carbonate of potash, lixiviating, and precipitating it by nitric acid, was procured in the state of a white powder, not very heavy, having scarcely any taste, not soluble in boiling water, but which, when placed on litmus paper, mixed with distilled water, renders the paper red. Exposed to a strong heat for an hour and a half, imbedded in charcoal, it became black; but by a heat so intense as to have melted the crucible, no metal was obtained. Heated with borax, it remained equally infusible, but with phosphate of ammonia an effervescence took place, and a globule was obtained when cold of a deep blue, which, held between the eye and the light, appeared of a greenish grey colour. This substance Mr Hatchet found to be insoluble in nitric acid, even

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* Journal des Mines, tom. xii. p. 256. Nicholson's Journal, 8vo, vol. iii. p. 251.

when the acid is boiled on it. It dissolved by boiling sulphuric acid, and formed a colourless solution, decomposed by water. Muriatic acid boiled on it, likewise dissolves it, and this solution may be diluted with water without decomposition. Phosphoric acid, added to these solutions, produced a copious flocculent precipitate. The alkalis threw down a white flocculent precipitate. Prussiate of potash changed the colour to an olive-green, and a precipitate of the same colour gradually formed. Tincture of galls produced a deep orange-coloured precipitate. The fixed alkalis combined with this metallic oxide, a compound being formed soluble in water, and affording with an excess of alkali, by evaporation, a substance in shining scales, not soluble readily in cold water; and from which nitric acid precipitated the oxide. Prussiate of potash and tincture of galls produced no change; but when with either of them a few drops of muriatic acid were added, precipitates similar to those produced by these re-agents in the acid solutions, appeared,—an olive-green with the one, and an orange-coloured precipitate with the other. Hydro-sulphuret of ammonia produced a reddish-brown precipitate. The oxide is not soluble in ammonia.

In many of these properties there is evidently a nigh resemblance to the oxide of tantalum of Ekeberg. But there is an important difference in others, particularly in the solubility of the substance described by Hatchet in sulphuric and muriatic acid, and the colour it gives to phosphate of soda. Dr Wollaston, however, examining again the specimen which had been analysed by Mr Hatchet, found the oxide obtained from it to be less soluble in acids; and in all its properties to be nearly the same with oxide of tantalum. What appeared to establish their identity, he found both of them to have the peculiarity of being dissolved completely by oxalic, tartaric, and citric acids *.

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* Philosophical Transactions, 1809.

Berzelius states, that Ekeberg had found the columbic acid, as it has been called, to be oxide of tantalum with tungstic acid, to which latter substance it owed its peculiarities, and this is apparently confirmed by tungsten being found naturally associated with tantalum *.

Berzelius has lately submitted to analysis a variety of minerals found in Sweden, containing tantalum as a principal ingredient, combined or mixed with oxides of iron, tin, manganese, and tungsten. And he has added a number of important facts to the history of this metal, and its compounds †.

He succeeded in reducing it to the metallic state, by submitting the oxide in a cavity of calcined charcoal, with charcoal covering it, in a Hessian crucible, to the heat of a forge for an hour. A metallic mass was obtained, preserving the form of the cavity, but contracted about a fourth of the volume of the oxide. The heat necessary to the reduction is about as high as that required for oxide of manganese, and it was not possible to melt the metal. The grains, however, adhered strongly together; the porosity did not admit of the specific gravity being determined; the smaller grains were hard, so as to scratch glass. The colour was a deep grey; rubbed on a hammer, the mass acquired metallic lustre, similar to that of iron. When reduced to powder, it has none of this lustre. When heated to perfect redness, it burns weakly without flame, and assumes a greyish white colour, but it is not possible to convert it completely into the white oxide. Heated with nitre it deflagrates feebly, and the residue, which is of a snow-white colour, is a compound of the oxide with potash.

Tantalum appears to be susceptible of only one degree of oxidation. The best mode, according to Berzelius, of

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* Annals of Philosophy, vol. iv. p. 467.

† Annales de Chimie et Physique, tom. iii. p. 140.

obtaining the oxide pure, is to fuse it in a platina crucible with carbonate of potash, and lixiviate the mass in water; the excess of alkaline carbonate is first removed; the remainder dissolves in boiling water. Muriatic acid added to the solution, precipitates the oxide of a white colour. If digested with an excess of acid, and then washed with boiling water, until nitrate of silver gives no opacity, a bulky powder is obtained, which is the hydrated oxide. It reddens litmus paper, and this even after it has been dried, if the paper is moistened. When heated in a retort, the water it contains is expelled; this water shews no acidity; the reddening property, therefore, is not owing to the presence of any foreign acid, but, as Berzelius remarks, must be ascribed to the oxide itself; yet this oxide, when the water is abstracted from it, has no such power. This affords an excellent illustration of the view which I have proposed, that the combination in such cases is that of the elements of water, not water itself, and that the acidity is to be ascribed to the joint operation of the oxygen and hydrogen on the metallic radical.

In the pure oxide free from water, Berzelius found reason to infer, that 100 of metal are combined with 5.485 of oxygen; it is composed, therefore, of 94.8 of tantalum, and 5.2 of oxygen. The hydrate contains in 100 parts, 10.5 of water; or probably consists of other two proportions of oxygen, with an equivalent proportion of hydrogen. As in this state it reddens litmus, does not combine with acids, and unites with alkalis, earths, and metallic oxides, there is certainly sufficient ground for distinguishing it as a metallic acid.

This tantalic acid exposed to ammonia, absorbs a quantity of it; and if this tantalate of ammonia is mixed with the solution of an earth or a metallic oxide in an acid, an interchange takes place between the principles of the two salts, and different tantalates may thus be obtained.

Metallic tantalum, even in the state of powder, is not affected by muriatic, nitric, or nitro-muriatic acid; the last, even after several days digestion, produced no change. It is only by the action of an alkali, aided by heat, that it is oxidated.

The oxide even is equally incapable of being dissolved by acids,—nor is it, according to Berzelius, dissolved by oxalic, tartaric, or citric acid, as had been stated by Dr Wollaston; the hydrated oxide is dissolved in considerable quantity by boiling with super-tartrate of potash.

Potash is the proper solvent of oxide of tantalum. Soda, according to Dr Wollaston, dissolves it, even with the aid of heat, much more sparingly, and the greater part of the oxide separates from the solution in cooling, in combination with part of the soda. The solution in potash is not precipitated by infusion of galls, prussiate of potash, or hydro-sulphuret of potash; but if a sufficient quantity of acid be added to remove the excess of alkali, preserving neutralization, the infusion of galls occasions an orange precipitate; the other two re-agents form no precipitate. Infusion of galls, therefore, is the characteristic precipitant of this metallic oxide. When poured on the oxide itself, newly precipitated and still moist, it combines with it, and forms the orange-coloured compound.

Tantalum does not combine with sulphur. According to Berzelius, it is capable of combining with the metals; but these combinations have not been examined.

CHAP. XXVII.

CERIUM.

A FOSSIL found at Bastnaës in Sweden, and regarded as a variety of wolfram, had been analysed by Scheele and D'Elhuyart, but without any certain results. The former chemist not obtaining tungsten from it, named it False Tungsten. It was submitted to examination by Messrs. Hesinger and Berzelius, and the result was the discovery of a new metallic oxide, the properties and combinations of which they described *. The same mineral had been operated on by Klaproth, who extracted this oxide from it, and considered it as an earth, to which he gave the name of Ochroites †. Vauquelin also undertook the examination of this substance, confirmed the discovery of the Swedish chemists, and reduced the oxide to the metallic state ‡. This metal received from its discoverers the name of Cerium; and they gave the name of Cerite to the fossil in which it is contained; it consists of oxides of cerium and iron, with silica and lime. Dr Thomson discovered oxide of cerium in another mineral, which he named Allanite, in which it is also combined with oxide of iron, silica, and lime ||; and it has since been found by Berzelius in the gadolinite and some other fossils, combined with ittria and with fluoric acid.

The pure oxide of cerium is extracted from the cerite,

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* Nicholson's Journal, vol. ix. p. 290.

† Ibid. vol. viii. p. 207.

‡ Annales de Chimie, tom. liv. p. 28.

|| Transactions of the Royal Society of Edinburgh, vol. vi.

by dissolving this mineral in nitro-muriatic acid, and, after saturating the solution with an alkali, precipitating by tartrate of potash. The precipitate well washed, calcined, and digested in vinegar, is oxide of cerium. It is difficult to free it from oxide of iron; this is completely effected by a method given by Laugier,—dissolving the cerite in nitro-muriatic acid, precipitating by ammonia, and after washing the precipitate, pouring on it, while humid, a solution of oxalic acid; the oxide of iron is dissolved; and the oxalate of cerium remains insoluble; calcined by a red heat, it affords the pure oxide *.

Vauquelin, after a number of unsuccessful trials to reduce this oxide, obtained a few metallic grains, by exposing the tartrate of cerium with lamp-black, oil, and borax, to an intense heat. These did not amount to a fiftieth of the cerium employed; and hence he concluded, that it is volatile at a very high heat. They were too minute to admit of the properties of the metal being accurately determined. By exposing the oxide to the action of potassium, Sir H. Davy found potash to be formed, and a deep grey metallic powder was obtained. Mr Children, on submitting oxide of cerium to the intense heat of his large galvanic battery, found it to melt, and to be partly volatilized, burning with a vivid white flame, but without being reduced. Laugier found, that the metal or its oxide is not volatile at an intense heat in close vessels. In attempting its reduction by charcoal, he obtained a black shining matter, in which the metal was combined with carbon, in the same proportion as that of the oxygen with which it had been united.

Oxide of cerium, it is remarked by the Swedish chemists and by Vauquelin, exists in different degrees of oxidation. When precipitated from its acid solutions by the alkalis, it is white, but acquires a shade of yellow when

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* Annales de Chimie, tom. lxxxix. p. 517.

dried in the air, and, when exposed to a continued heat, becomes of a brick-red colour. The white, according to Vauquelin, is the one at the lower degree of oxidation. Neither of them can be fused by heat. Borax determines their fusion; the globule, heated by the exterior flame of the blowpipe, is of a blood-red colour, which, by cooling, becomes of a yellowish-green, and at length colourless and transparent, or, if the proportion of oxide has been large, opaque and pearly.

As the degrees of oxidation cannot be determined directly from experiments on the metal, Hisinger endeavoured to determine them from the quantity of acid in its salts. The protoxide, he inferred, is composed of 88.1 of metal, and 14.9 of oxygen, or 100 with 17.41; and the peroxide of 79.3 and 20.7, or 100 with 26.1 *.

The metal itself, in the trials which Vauquelin made with it, proved insoluble in any unmixed acid, and was dissolved with difficulty in nitro-muriatic acid. Its oxide, however, combines with the acids easily, and forms salts which have a sweetish taste.

The oxide, at the minimum of oxidation, dissolves in sulphuric acid: the solution is colourless, or of a very light-red tinge, of a sweet taste, and by evaporation affords white crystals. When the oxide is at the maximum, it is dissolved with more difficulty: it requires the aid of heat, and dissolves more readily when the acid is diluted with from 4 to 7 parts of water, than when it is concentrated: the solution is of an orange colour, and by evaporation affords small prismatic crystals of the same colour. In re-dissolving these crystals in water, they are partly decomposed, and a white powder precipitated, which is a sub-sulphate of cerium, while a super-sulphate remains dissolved, which by evaporation may be obtained in small prisms.

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* Annals of Philosophy, vol. iv. p. 355.

Nitric acid dissolves the white oxide of cerium: the solution has a sweet taste, with a degree of sharpness: it does not easily crystallize. The acid dissolves the red oxide with difficulty in the cold, but with heat more easily: the solution is of a yellowish green colour. If there be an excess of acid, white crystals are obtained on evaporation and cooling, but the neutral solution becomes only of a thick consistence by evaporation: alkohol dissolves this matter, forming a red coloured solution.

The red oxide of cerium is slowly dissolved by muriatic acid in the cold, and more readily by heat; and oxymuriatic acid gas is disengaged with effervescence. The colour of the solution is a faint greenish yellow; evaporated to the consistence of honey, it affords a confused crystallization; the saline matter is deliquescent; it is soluble in its weight of cold water, and in three or four times its weight of alkohol.

Phosphoric acid digested with oxide of cerium, forms an insoluble salt. It combines with carbonic acid, when water saturated with that acid is poured on it; and when humid, it attracts carbonic acid from the atmosphere. The compound is insoluble. Both the phosphate and carbonate are easily formed by complex affinity.

The salts of cerium are decomposed by the alkalis, and a precipitate thrown down, which appears to be a sub-salt. If an excess of acid be present, triple salts are formed. The saturated solutions of cerium are precipitated white by prussiate of potash. Gallic acid gives a very small quantity of a white precipitate, which is increased, and becomes brown when any excess of acid is removed by an alkali. Hydro-sulphuret of ammonia produces a brown precipitate, and a deep green one when a larger quantity of the hydro-sulphuret is added. Hydro-sulphuret of potash forms at first a green precipitate, which, according to Vauquelin, arises from the presence of iron: when this has subsided, and a fresh quantity of the hydro-sulphuret is added, the precipitate is white: it appears to contain no sulphuretted hydrogen, as it dissolves in acids without any effervescence; and hence the oxide of cerium neither combines with sulphuretted hydrogen, nor is reduced by it. Phosphorus put into a solution of muriate of cerium throws down gradually a white precipitate. The solutions of cerium are not precipitated by iron or zinc.

The pure alkalis do not dissolve cerium, even by fusion. Ammonia, digested with the oxide, does not dissolve it, but renders it yellowish. The carbonated alkalis dissolve it in small quantity in the humid way, and likewise by fusion, forming triple salts.

It appears, from the result obtained by Laugier, stated above, to combine with carbon. The carburet he found to inflame spontaneously, when exposed warm on paper to the atmosphere, and the red oxide remained.

CHAP. XXVIII.

SELENIUM.

This is a very singular substance, lately announced as discovered by Berzelius. In a manufacture of sulphuric acid at Fahlun in Sweden, the sulphur employed is obtained by sublimation from copper pyrites. Gahn and Berzelius observed a deposite of a reddish coloured matter in the chamber, composed partly of sulphur, but which, when heated, gave a strong smell, similar to that of horse-radish, from which they suspected in it the presence of tellurium. Berzelius having submitted it to more particular examination, succeeded in separating the sulphur, and obtaining the body, to which, from the analogy of the name tellurium, he gave the name of Selenium. Its claim to be ranked as a metal may be considered as doubtful, for it softens at a moderate heat, and becomes ductile, so as to be drawn into threads, which are transparent; it is a very imperfect conductor of heat, and a non-conductor of electricity. It is heavy, however, has the metallic lustre, and in the greater number of its chemical properties is similar to metals. The following account of it is given from the abstracts of the Memoirs of Berzelius hitherto published * :

Selenium is of a grey colour, with a brilliant metallic lustre: when broken it has somewhat of a red tinge; it is hard, but easily frangible like sulphur, and like sulphur also has the vitreous fracture: its specific gravity is about 4.6.

At the temperature of boiling water it softens, and when the heat is raised a little higher it melts. In cooling it retains a degree of softness and tenacity, so that it can be kneaded or stretched into threads of great fineness; these, when held between the eye and the light, appear transparent, and of a dark red colour; by reflected light they exhibit high metallic lustre. When cooled hastily it has a vitreous fracture, with scarcely perceptible lustre: when cooled slowly, the fracture is granular, like that of a metal.

At a temperature approaching to that of boiling mercury it is volatilized, boils even, and may be distilled over in opaque metallic drops; the retort is filled with a yellow vapour, similar to that of sulphur, but less intense. Sublimed in a large vessel, it condenses in a light sublimate of a fine cinnabar colour, which, when fused, forms the usual grey coloured metallic mass. When sublimed in the open air without taking fire, it evaporates in a white smoke, which is destitute of smell. But when heated in

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* Annales de Chimie et Physique, tom. vii. p. 199. Annals of Philosophy, vol. xi. and xii.

the flame of a candle, or before the blowpipe, it burns with an azure blue tinge in the flame, and exhales a very pungent smell, similar to that of horse-radish, but so strong that the fiftieth of a grain is sufficient to diffuse it through the air of a chamber. The smell of the vapour of tellurium is similar, but much weaker.

Selenium is dissolved by acids. Nitric acid dissolves it easily when assisted by heat. The solution evaporated in a retort leaves a crystalline mass, which sublimes in long crystalline needles. This substance is unequivocally acid. It is very soluble both in water and in alkohol: its taste is purely acid, it reddens litmus, and it combines with the alkalis, forming salts. Berzelius names it Selenic Acid, and its salts Seleniates. The alkaline seleniates crystallize with difficulty, and attract moisture from the air: that of ammonia is decomposed by heat, a little ammonia is disengaged, after which the selenic acid sublimes; but the greater part of the ammonia is decomposed, nitrogen gas is evolved, and water formed, and selenium remains. Seleniates of barytes and lime are soluble in water; that of barytes crystallizes in needles. If muriatic acid is added to a solution of a seleniate, and a plate of zinc be introduced, selenium is precipitated in red flocculi. If this experiment is performed with sulphuric acid, sulphuret of selenium is formed, of a grey colour. Sulphuretted hydrogen passed through an aqueous solution of selenic acid, causes a precipitate of an orange colour, which becomes red in drying, and when heated melts, sublimes, and forms an orange coloured transparent mass.

Selenium combines with the alkalis, both in the humid way and by fusion, forming compounds, alkaline selenurets, of a red colour. Those of barytes and lime are of the same colour, but are insoluble in water. Like sulphur it dissolves in the oils, but the solutions have no hepatic smell.

With the metals it combines, the combination being generally attended with the phenomena of ignition. Its alloys have usually a grey colour, and metallic lustre. Seleniuret of potassium dissolves in water without effervescence; the solution has a taste similar to that of sulphuret of potash. The acids disengage from it seleniuretted hydrogen gas, which has an odour when diluted similar to that of sulphuretted hydrogen, but is intolerably more offensive, exciting, if received into the nostrils even in small quantity, a very painful sensation, followed by inflammation and catarrh. It is soluble in water, combines with the alkalis, and precipitates metallic salts. In these and other properties, the analogy of selenium to sulphur is very striking. It appears to form the link which connects the simple inflammables with the metals.

Selenium no doubt exists in the metallic sulphuret from which the sulphur with which it is associated is extracted. It is not contained in the acid prepared from this, its presence being prevented by its property of being precipitated in the state of a sulphuret.

BOOK VII.

OF MINERAL COMPOUNDS.

The general name of Mineral Compounds, applied in contradistinction to Vegetable and Animal Compounds, may be given to the substances formed by the combinations which exist in the Mineral kingdom. They are usually compounds of Acids, Alkalis, Earths, Metals, and Inflammables. Their discrimination and description belong to a different branch of natural knowledge, Mineralogy; but still Chemistry is connected with this by certain relations, and the just extent of these requires to be illustrated in a few preliminary observations, as affording the point of view under which this department of the science is to be surveyed.

It is obvious that, as a material substance, every mineral is an object of chemical research; its nature must be determined by analysis, and its chemical properties and relations must be assigned. But minerals display the peculiarity, that they exert few chemical agencies; they are composed of elements, the affinities of which are in general not energetic; these affinities are weakened by mutual combination; and any action that might arise from them, is farther counteracted by the state of aggregation. Hence they scarcely enter into any combination; nor do they cause any important decomposition; and of all bodies they may, in respect to chemical powers, be regarded as the most inert.

From this character arises the peculiar point of view under which they are regarded. Their chemical properties, as they are so few and unimportant, are insufficient to discriminate them with sufficient facility and precision, and their distinctions are more frequently established from their physical characters. This leads to a very minute discrimination of these characters; and hence, strictly speaking, mineralogical description comprises little chemical investigation.

But there is another point of view under which chemistry and mineralogy are more intimately connected. The nature of minerals can be determined with certainty only by chemical analysis; and it is only from difference of chemical constitution, that essential distinctions among them, in common with all unorganized bodies, are established. In organized beings, such distinctions are dependent on a different source,—on peculiarities of structure and organization, connected with the functions of life; these form, therefore, the proper basis of specific characters among vegetables and animals. But in minerals such peculiarities are totally wanting; the only source of real distinction, that is, of identity or difference of nature, is chemical constitution, and this therefore must constitute the basis of the Mineral Species.

This has been admitted in the principal Systems of Mineralogy, but not altogether without limitation; and the mineralogical arrangements of the present day are even founded to a considerable extent on other principles. Werner remarked, that the foundation of the mineral species is an agreement in the relations of the constitution of minerals, defining at the same time this constitution to be the combination of their constituent principles; but in the details of his system this principle is often departed from, different species being formed where there is no essential difference of composition, and minerals being often grouped in opposition to chemical distinctions or alliances. And Hauy, although admitting the necessity of recognising the chemical composition in his definition of a species, places it as subordinate to a distinction drawn from a different source,—the form of the integrant molecule; and frequently disregards it, when placed in opposition to the character which he thus combines with it.

In the Wernerian system, the species of minerals are in general determined from their external characters. The qualities of colour, transparency, lustre, form, structure, hardness, and specific gravity, display a certain assemblage of characters, which, exhibited by all the individuals of a species, admit of its being recognised; they form, therefore, the type or indication of the species; and from such characters the greater number of species, it is maintained, can be established, independent of their chemical constitution.

In the system of Hauy, the specific character is derived from the crystalline structure of minerals. In delivering the theory of crystallization (vol. i. p. 44.) it has been remarked, that in every crystallized substance, a common form exists in all the varieties of its crystals, which may be extracted by mechanical separation. If the actual crystal be attempted to be divided by a force applied to it in certain directions, it will not yield so at least as to present fragments with smooth surfaces; while, if struck in a different direction, it will split readily, and give fragments having this character. This indicates the natural joints of the layers, the aggregation of which forms the crystal, and by following these the crystal may be divided; and as the result of its division, will at length present a nucleus of symmetrical form. Hauy found, that in all the varieties of crystals of the same mineral, however much they may differ in their actual forms, the same primitive form may be extracted; that from the numerous varieties, for example, of crystallized carbonate of lime, a rhomboid is obtained, having its angles invariably the same,—from those of fluate of lime, an octohedron is obtained, and from sulphate of lime a four-sided prism. This nucleus may be farther divided, parallel to its different faces, and sometimes in other directions: and this subdivision, it is demonstrable, might be carried on, did the minuteness of the solid allow us to operate on it until it were reduced to a particle composed of the elements of the substance, and which of course could not be separated without chemical decomposition. This Hauy denominates the integrant molecule; it is of certain regular geometric forms, different in different substances; it varies, too, in the dimensions of its form, or in the measures of its angles, but is constant in all the varieties of the same crystallized substance. He regards it, therefore, as affording the proper basis of specific distinctions in the mineral kingdom: And according to his definition, a mineral species may be said to be *a collection of bodies, of which the integrant molecules are alike, and composed of the same elements united in the same proportions;* this latter condition being added, as he remarks, to generalize the definition, and extend it to substances, which, having their integrant molecules of the same form, differ essentially in the principles of which these molecules are composed [*].

With regard to the Wernerian principle of arrangement, no doubt can remain of the great value of the external characters of minerals in affording signs by which the species may be recognised, nor of the skill with which they have been applied to this purpose. But still they do not properly constitute a basis of specific distinction. The peculiarity with regard to the substance, which gives rise to the assemblage of characters, whatever it may be, is what forms this basis. Now this can be nothing but its peculiar nature or constitution. Some of these characters

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[*] Traité de Mineralogie, tom. i. p. 162.

indeed arise immediately from mechanical structure or aggregation, but this is itself the result of the composition of the body; and it is this composition which, under all the varieties of structure in the different varieties of the same species, remains essentially the same. Where it can be discovered, therefore, it is what defines the species with greatest precision. And even considering the external characters only as affording the indications of the species, they afford a criterion which must always be to a certain extent arbitrary and uncertain;—arbitrary, as being dependent on the rules that have been followed in selecting the distinctive characters, so that if different rules were followed, different groupes would be formed;—uncertain, as important diversities of properties may arise in a combination, from circumstances trivial and accidental. So far as the individuals which are of similar composition are placed together, the system is a natural one; and in the diversity of systems that might be formed, a number of the species, were the external characters alone to be attended to, would thus be found the same. But this is only from the circumstance, that similarity in composition in general gives rise to similarity of properties; and hence allows, even on the principles on which such arrangements are constructed, a number of natural species to be formed. Where this is not present, and where the external characters, instead of being regarded as subordinate to the chemical relations, are placed in opposition to them, and considered as the basis of the classification, the arrangements, whatever excellence they may possess as descriptive, are altogether artificial, and must deviate widely from the real specific distinctions.

The same observations nearly apply to the other system, that in which the mineral species is established on the primitive form of the crystals. As a character enabling us to recognise the species, its utility may be admitted. There is often a difficulty in doing so, either by the aid of chemical analysis, or by observance of the external characters of minerals; the character drawn from the structure of these in their crystalline forms, is a very important one; and apparently intimately connected with peculiarity of composition, may often be employed with advantage; and as Hauy remarks, "where it shews itself, there is a ray of light against which we ought not to shut our eyes." But it cannot constitute the proper specific distinction. The identity of this primary form in the different varieties of the same substance, must itself arise from some cause, from something peculiar to the substance to which it belongs. It is this, whatever it may be, which properly constitutes the base of the species; the identity of form is only a sign by which it is recognised; and what can this be, but identity of chemical composition? Hence, by discovering the exact composition, we establish the species, independent of these researches on the form of the molecule, and this even where, from the absence of crystallization, or from any other circumstance, that form with its accompanying relations cannot be discovered. The insufficiency of the form of the integrant molecule alone for this purpose, is apparent from the admission of the fact which renders the qualifying condition necessary, that mineral species, totally distinct, have frequently the molecule of the same form. And although Hauy has remarked, "that the greater number of substances which have a common molecule, are easily distinguished by other characters," this, independent of the admission implied in it, that the character from the form of the molecule is defective, is no necessary circumstance; on the contrary, there is no cause why two species closely allied in their external characters, may not have a similar alliance in the form of the primitive molecule. In such a case, according to this system, we should either be obliged to have recourse to chemical analysis, or to some other character, to distinguish them; or we must confound, under one species, what are essentially distinct. And accordingly, there are several examples in Hauy's system, of a mineral important from its uses, extremely different from others in its external characters, and even in its composition, being ranked merely as a variety, because its difference of form is not regarded as sufficiently important to constitute it a species. The deficiency of this method is not less apparent in the circumstance, that many fossils, well characterised as species, do not occur crystallized, and therefore, either cannot be arranged under it, or, in defiance of their real distinctions, must be placed as varieties of other species, which happen to exist in a crystallized state. And even the very basis of the system has been called in question by the observation, that the crystalline structure may be developed under very different modifications, and that thus, with regard to the same substance, different primitive powers may be, and have been assigned *.

The conclusion which may be drawn from the preceding observations is, that chemical composition is the basis of the mineral species; a combination uniform, or nearly so, with regard to ingredients, and to the proportions in which these are combined, constituting a species; and thus as many species being formed as there are combinations sufficiently definite and uniform in the mineral kingdom.

At the same time, in the application of this principle difficulties undoubtedly occur. From the analyses that have been hitherto executed, it is found that minerals, which, from their strict resemblance in external qualities, appear to belong to the same species, frequently differ considerably in composition; the proportions of the ingredients are variable, and sometimes even there is a diversity in their constituent parts.

These difficulties arise from the imperfections of mine-

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* Journal de Physique, 1807.

ral analysis. The composition of minerals is often complicated, consisting of four, five, or more ingredients.—The methods of analysis by which these are separated, and their quantities estimated, are liable to numerous sources of error; and hence, therefore, there is every reason to believe, the inaccuracies of experiment are far from being unfrequent or unimportant. There is another difficulty in the selection of specimens submitted to analysis, the real composition being often disguised by mechanical intermixture, and this even in minerals apparently homogeneous and crystallized. On the other hand, the action of some substances seems so energetic, that the presence of a minute portion of them determines the specific characters, while others may be present to a much greater extent without an equal influence; and as these combinations are not perfectly definite, a variable quantity of such ingredients may exist in a specific composition, without giving rise to much modification of properties. Lastly, the state of aggregation often modifies the physical properties, and thus conceals or renders doubtful the identity of species. These sources of error will be only slowly remedied, so as to admit of the real composition in each species being unequivocally established.

It is of importance, however, to remark, that with regard to many minerals, this has been already accomplished. Nearly all the metallic minerals may be determined from chemical analysis alone, though in some of them difficulties may occur from gradation of composition or mechanical intermixture. How well defined, for example, as a species, is the carbonate or the phosphate of lead, and indeed all the native metallic salts? The metallic sulphurets are nearly equally capable of being thrown into distinct species from their composition, especially if attention is paid to the metal which is essential to it. The arrangement of the fossils of which three earths, lime, barytes, and strontites, are the bases, are at once fixed from their chemical composition; for who would refuse as species the sulphate of lime, or the carbonate or sulphate of barytes, or of strontites, or search for any other specific distinction than their chemical nature? If we take a specimen of one of these, suppose it to be sulphate of lime, it is in our power to analyse it with accuracy; and therefore we shall always be able to recognise it, whatever appearance it puts on. In one specimen it may be of a fibrous structure, in another foliated, in a third compact: it may be colourless or coloured, amorphous or crystallized. But under all these aspects, it is easy to discover the identity of these specimens by analysis, and hence they are to be regarded only as varieties of one species.

The minerals with regard to which the determination of the species from chemical analysis is least perfect, are those composed of different earths in combination with each other. There is an extensive series, for example, composed of silica, alumina, and magnesia, in combination with each other, with the addition often of metallic matter, particularly oxide of iron. In many of these, it is difficult to determine the real specific composition; different varieties which, from the general agreement in properties, evidently belong to one species, yielding results very different with regard to the proportions of the ingredients, and sometimes even with regard to the ingredients themselves. If the mineral Feldspar be selected as an example, it is found always to contain siliceous earth as its principal ingredient, and next to this, argillaceous earth. But the proportions of these are very various,—the silica varying from 60 to 70, the alumina from 12 to 17; and the composition is not less variable in the presence of other ingredients; in some specimens lime, magnesia, and even barytes, are present; in others they do not exist; and potash has been discovered in one variety, without being found in others. Now it is obvious, that from such analyses, it is difficult to determine what composition really constitutes the species Feldspar. The same difficulty exists with regard to many other fossils to an equal extent.

In relation to such examples, chemical analysis alone is obviously in its present state inadequate. Other methods of determining the species must therefore be at least provisionally employed; and thus a mixed system is introduced. The determination is founded frequently on the characters of the mineral displayed in its physical properties, aided as far as can be done by its chemical relations, and the results of its analysis. A mineral differing in the assemblage of its properties from all others, and displaying these properties with uniformity, is considered as a species. Feldspar, for example, is thus characterized by its peculiar lustre, its foliated texture, rhomboidal fragments, its crystalline forms, its degree of hardness, its specific gravity, and its degree of fusibility. Its composition is also assigned with as much precision as the results of its analysis admit. If another specimen occurs possessing the greater number of these properties, but differing somewhat in others, in colour, for example, or transparency, it is still regarded as of the same species. If its composition is even found to be somewhat different, this does not establish the conclusion, that it is a different species; the agreement in properties is more important, and the difference in composition is held to be unessential. In this manner the species is determined as much from resemblance in properties, as from the results of analysis; and a strict analogy in the former, is even admitted as sufficient to counterbalance a considerable discordance in the latter, and to refer different varieties to one species, though their composition may not be perfectly alike. It is at the same time obvious, that this does not invalidate the superiority of chemical analysis where it can be established, and ultimately the composition must in every case form the real basis of the specific distinction.

The method then which is applicable in the present state of chemical mineralogy, is to apply the distinction from composition, wherever it is applicable; and where it is not, to avail ourselves in the mean time of other characters, and to expect the perfection of the classification in the progress of chemical analysis. Where the species cannot be derived from composition, it must be formed from analogy in properties; and the skill of the Mineralogist has an ample field for exertion in seizing on those analogies which are most distinctive, and most intimately connected with identity of composition. Where a number of varieties agree in the possession of certain distinctive qualities, these ought to be considered at present at least as a species, though the composition which constitutes this may not be fully determined. But where the chemical constitution is unequivocally determined, it would be an error to disregard this, and establish the species on other characters. The propriety of establishing the species feldspar or garnet on external characters, is not to be questioned; for, in the present state of chemical analysis, we cannot assign the precise composition on which it is founded. But who can doubt of the composition of sulphate of lime, or barytes, or carbonate of strontites? Each of these is a proper species: there is no essential difference in composition, whatever difference there may be in properties, in the varieties of it which exist in nature; and to form any of these varieties into species, would be to create distinctions without any essential difference; or to derive the species itself from the properties, and not from the composition, is to relinquish a sure criterion, for one which must always be in some degree uncertain and vague.

The species being fixed on chemical composition, the genera and orders have necessarily the same basis, and on this principle the higher divisions have usually been established in mineralogical systems since the time of Cronstedt, by whom this arrangement was proposed. Each earth forms a genus, under which are associated the different minerals in which it is predominant. Each metal forms a similar division, under which its different ores are arranged, and the few inflammable bodies found in the mineral kingdom are arranged in a similar manner. Thus genera are established, and these again are united under the more comprehensive divisions of Saline, Earthy, Metallic, and Inflammable Minerals.

I have placed in the following sections all the well defined species of the mineral kingdom, in conformity to these views, stating the peculiar composition of each, so far as this is sufficiently determined. The details of mineralogical description I have abridged, as foreign to a system of chemistry. And I have done so the more readily, that it is my intention, in a separate publication, to deliver an Outline of Chemical Mineralogy. For more full descriptions, I refer to the System of Mineralogy by Professor Jameson.

From the importance of the external characters of minerals in their discrimination, it is necessary that the terms denoting them should be employed with the utmost precision. With this view, an accurate descriptive language was established by Werner,—I add the principal definitions belonging to this, referring to Mr Jameson's treatise on the External Characters of Minerals, for the entire system.

The principal external characteristic properties affording mineralogical distinctions are Colour, Lustre, Transparency, Form, Texture as displayed by fracture, Hardness, Tenacity, and Specific Gravity.

Colour.—To describe this with sufficient accuracy, the method adopted by Werner, is to select certain principal or standard colours, and to refer to these the subordinate shades, defining them by adding an epithet, either expressive of the intermixture of one of the principal colours with the other, or derived from some substance familiarly known, the colour of which is constant. The principal colours assumed are, *white*, *grey*, *black*, *blue*, *green*, *yellow*, *red*, *and brown;* and of these are subordinate colours, designated according to the above mode, as bluish-grey, greyish-black, blackish-green, snow-white, lead-grey, grass-green, &c. Even these are not always well marked, but *incline to*, are *intermediate*, or *pass* into each other. The shade of colour is also of different intensities,—dark, deep, light, and pale. The discrimination is often derived from the tarnishing of colours, where the colour of the surface is different from that which a fresh fracture exhibits; or from the play or the changeableness of colours, as the position is varied with regard to incident light. And numerous varieties are introduced from the delineation of colours, arising from an assemblage of different colours on the same surface, as dotted, stripped, zoned, &c. The colour is also sometimes varied by scraping the surface, affording a character named the STREAK.

LUSTRE denotes the relation which a fossil bears to the reflection of light from its surface. The degrees of it have been expressed by numbers, but defined terms are preferable; as with regard to qualities not admitting of exact measurement, it is difficult to attach precise ideas to numbers. In the Wernerian language, *resplendent* denotes the highest degree of lustre, such as is visible even at a considerable distance: *shining* is applied when the lustre, though perceived at a distance, is not so well observed as on a near approach: *weakly shining* or *glistening*, when it is perceptible only at a very short distance: *glimmering*, when some of the minute parts only of the surface reflect a weak light: and *dull*, when lustre is wanting. Different kinds of lustre are also marked, as the metallic, adamantine, vitreous, waxy, pearly, and resinous.

TRANSPARENCY.—To denote this property in its different degrees, numbers have likewise been applied, but defined terms are preferable. The following are employed:

Transparent, applied where objects can be distinctly perceived through the interposed substance: *semi-transparent*, where they are seen, but not distinctly, and this only through thin pieces: *translucent*, when light is transmitted, but objects cannot be observed: *translucent at the edges*, when the light is transmitted only through the thinnest edges or fragments: *opaque*, when no perceptible light is transmitted. Connected with the transparency is another characteristic property,—the Refraction, which in the greater number of minerals is single, but in some double, the latter giving a double image when an object is surveyed through them.

Form.—This includes the figures of crystals, and the particular forms which minerals assume even in their uncrystallized state. With regard to the first of these,—the forms of the crystals, sufficient details have been given under the history of Crystallization, in the first volume, to which I refer. The aggregation of crystals affords some distinctions, especially where they form groupes disposed in particular modes, as scopiform or fascicular, where slender crystals diverge from a common centre; acicular, where long needle-shaped crystals adhere laterally; manipular, fasciform or sheaf-like; pyramidal, &c.

Of the less regular, or Imitative forms, there are many varieties, named usually from resemblances to objects generally known; as capillary, or in fine threads; filiform, or like wire; dentiform, resembling teeth; reticulated, or like net-work; dendritic or arborescent, resembling branches; coralliform, like coral; stalactitic, consisting of conical shoots or projections: botryoidal, resembling a branch of grapes; reniform, mammillary, cavernous, &c.

The Structure or Texture of fossils, as discovered by their Fracture, affords a very important discriminating character. The fracture may either present a surface continuous or uninterrupted; or it may present a surface composed of an aggregation of distinct parts, by which the continuity is more or less broken. The former is named the *Compact*, the latter has been termed the *Jointed* Fracture; and each is subdivided. Of the COMPACT, we have,—the *Splintery*, where, on a surface, even or nearly so, small splinters or scales are perceptible, adhering to the mass, and so thin at their edges as to be visible by the light transmitted, the scales being greater or smaller, and thus giving rise to the distinctions of coarse and fine splintery:—the *Even*, where the surface is smooth or destitute of elevations, or at least where the inequalities are few and indeterminate: the *Conchoidal*, where the surface is composed of concave and convex round elevations and depressions:—the *Uneven*, in which the continuity of the surface is interrupted by irregular elevations and depressions, usually angular, forming, according to their size, what are named coarse grained and fine grained:—the *Earthy*, where the surface is rough, from a number of small elevations and depressions: and, lastly, the *Hackly*, presenting small sharp-pointed elevations, and peculiar to the metals. The JOINTED Fracture, which is opposed to the Compact, is subdivided into the Fibrous, the Striated, and the Foliated. The Fibrous is where a number of parts like lines are discernible, which may be coarse or delicate, straight or curved, parallel, diverging, or promiscuous. The second, or the *Striated* or *Radiated* Fracture, consists of long and narrow aggregated planes, and differs from the former principally in these planes being of such a size that their surface can be distinctly perceived; being equal in breadth sometimes to one-fifth of an inch, and from this graduating into the fibrous. The striæ may be straight or curved, parallel, diverging or promiscuous. The last variety is the *Foliated* or *Lamellated* Fracture, which is composed of planes sufficiently distinct, the length and breadth of which are nearly equal. These may vary,—1st, In magnitude; the plates sometimes extending through the whole mass, and from this lessening to very small scales:—2d, In perfection; the fracture being either perfectly foliated, where the plates separate smoothly from each other; imperfectly foliated, where they separate unevenly, and with rather less lustre and smoothness than in the preceding; or concealed foliated, where they appear only in a few places, and are indistinct:—3d, In direction; the folia being either straight or curved: and, 4th, In passage or cleavage, by which is meant the property of splitting in certain directions; some fossils splitting only in one direction, when they are said to have a single cleavage; some in two, when they are said to have a double cleavage; some in three directions, in four, or even in six.

The Slaty has been distinguished from the foliated fracture by the parts possessing greater thickness, and not being capable of subdivision into very thin plates, splitting only in one direction, and separating with less smoothness. It forms the transition into the compact.

The shape of the Fragments of a Fossil frequently afford a discriminating character, as, in breaking, some fossils give fragments always of the same shape. They may be regular, as cubical, rhomboidal, pyramidal, and trapezoidal; or irregular, as cuneiform, specular, tabular; or altogether indeterminate.

Another character connected with the structure of fossils, is the appearance of Distinct Concretions, divided by natural interstices or joints, and therefore capable of being separated without breaking the mass; or, if they are more closely aggregated, discoverable by their different positions. With regard to shape, they are distinguished into, *Granular* distinct concretions, which may be round or angular, large, coarse, small or fine;—*Lamellar* distinct concretions, which may be straight or curved, thick or thin;—*Columnar* distinct concretions, which may also be straight or curved, thick or thin, perfect, imperfect, or wedge-shaped, parallel, diverging, or promiscuous.

HARDNESS in a fossil is judged of with most certainty by the comparative facility or difficulty of impressing it. Four degrees are marked by Werner :—*Hard*, in which the substance is not capable of being scratched by the knife, but gives sparks more or less plentiful when struck with a piece of steel; it may not yield to the file, when it is said to be extremely hard; or it may yield with difficulty, suffering a slight impression, when it is said to be very hard; or, lastly, it may be scratched by the file without difficulty, when it is said to be hard: *semi-hard*, when it does not strike fire with steel, and may be scraped by the knife: *soft*, when it may be easily scraped with the knife, but receives no impression from the nail: and *very soft*, when it is scratched by the nail. Haüy estimates the degrees of hardness according as one fossil impresses another: some scratching quartz, others calcareous spar, &c.

TENACITY is that property which relates to the cohesion of the integrant particles of minerals, and which, in different degrees, gives rise to the distinctions of brittle, malleable, and the intermediate degree of sectile.

The FRANGIBILITY is different both from hardness and tenacity, and denotes the facility with which a mineral may be broken. It exists in different degrees, which are marked by the common terms of difficultly frangible, easily frangible, &c.

SPECIFIC GRAVITY.—This property is determined with most accuracy by the hydrostatic balance. As this cannot always be practised, Werner gives degrees of specific gravity so general, that they may be estimated by poising the mineral in the hand. These are *supernatant*, applied to minerals of less specific gravity than water, and which therefore swim on its surface: *light*, the specific gravity of which is between 1000 and 2000: *rather heavy*, in which it is between 2000 and 4000: *heavy*, where it varies from 4000 to 6000: and *very heavy*, including all those fossils, the specific gravity of which is above 6000. The degrees are also stated more accurately by numbers in the usual manner.

To these characters are added a few of less importance, derived from properties peculiar to some minerals, such as that of adhering to the tongue: soiling the finger; feeling hard, or unctuous; giving a streak on paper; emitting, when struck, a peculiar sound; feeling cold when applied to the tongue; having taste; or exhaling perceptible odour.

The Chemical Characters of fossils afford important aid in discriminating them, and in fixing the species.

The Fusibility is generally determined by the action of the blowpipe, as we can thus operate on a small fragment, and perceive easily the appearances presented on fusion. Some minerals are infusible by it; others melt with facility: some fuse with intumescence; others decrepitate or exfoliate when urged by the flame, or lose their colour; in some the fusion is partial; sometimes the result is a kind of scoria; in many cases it is a complete vitreous globule, transparent, or opaque, and of various colours. These appearances are diversified by adding to the substance, which is the object of experiment, various fluxes, particularly borax and the phosphate of soda and ammonia; and observing the modifications of colour from the interior and exterior flame. The volatility of minerals by heat is determined by similar experiments, and attention is paid to the appearance of the vapour, its odour, &c.

The action of acids affords another important chemical character of fossils, by observing whether they effervesce when touched with the acid, or whether, when a small fragment is immersed in it, it is partially or entirely dissolved; if the solution is fluid or gelatinous; and what appearances it presents from the action of re-agents. Diluted nitric acid is generally used in these trials. And farther information is obtained by adding to a minute portion of the solution, a drop or two of the different chemical precipitants.

To the characters taken from certain physical properties, are referred the Phosphorescence, Electricity, and Magnetism of minerals. Phosphorescence is peculiar to some minerals, and therefore assists in their discrimination. In some it is excited by attrition, in others by heat. The electrical state, either positive or negative, is excited in some minerals by rubbing, in others by heat. And iron in many states of combination is discovered by its magnetic power.

Lastly, advantage is taken in the discrimination of minerals, of what are named Empirical Characters; of which the most important is that derived from natural association; some being frequently found in the same situation, and even blended with each other, while others are not observed to occur together.

CHAP. I.

OF SALINE MINERALS.

UNDER this order are placed those minerals which have the distinctive chemical properties of Salts,—which are uninflammable, sapid, soluble in water, and in general capable of assuming from their aqueous solution, a crystalline form. It includes one or two acids which are found native, and certain salts having alkaline, earthy, and metallic bases: and which may be arranged under genera, according to these chemical relations. One salt chiefly, Muriate of Soda, is a proper mineral substance, the others are either volcanic products, or are formed by processes carried on at the surface of the earth.

SECT. I.

NATIVE ACIDS.

Boracic Acid.—This is the principal substance belonging to this genus. It was first discovered in solution in certain hot springs in Tuscany, at the edges of which also it is found in stalactitic encrustations, or crystalline grains. Mr Tennant observed it adhering to some volcanic products from the Lipari islands; and Dr Holland since found it in considerable quantity, forming loose encrustations, adhering to the sulphur within the crater of Vulcano. It is distinguished by its acidity, its easy fusibility, and its communicating to flame a green tinge.

Sulphuric Acid.—This acid has been discovered in the glacial state in volcanic fissures and caverns, probably deriving its solid consistence from impregnation with Sulphurous Acid, which is a common product of volcanic operations, or from combination with sulphur. It can only be an occasional product, as from exposure to the atmosphere, it must soon attract moisture and be dissolved.

SECT. II.

ALKALINE SALTS.

Under this division may be placed those salts in which the alkalis are bases, combined with different acids. They are distinguished by their solution affording no precipitation on the addition of an alkali.

Muriate of Ammonia, or Natural Sal-Ammoniac, is always the product of volcanoes, or pseudo-volcanoes, being probably formed by the action of heat on substances containing its elements, and sublimed. It occurs as an efflorescence, loose and flaky, or in tuberose or botryoidal masses, of a greyish or yellowish white colour; its taste is acrid; it is abundantly soluble in water, and is easily distinguished by its chemical characters, being volatilized when heated, and exhaling a smell of ammonia when rubbed with lime. Sulphate of ammonia is mixed with it; and frequently also sulphur. A variety of the natural sal-ammoniac of Bucharia, Klaproth found to consist of muriate of ammonia 97.5, sulphate of ammonia 2.5. A variety from Vesuvius consisted entirely of muriate of ammonia with ½ per cent. only of muriate of soda.

NITRATE OF POTASH, Native Nitre, though referred to mineralogical systems, can scarcely be regarded as a mineral production, since it is formed only at the surface of the earth, and by operations which depend on the action of the air. It occurs as an efflorescence on the soil in warm and dry climates, particularly in India; and in Spain and Hungary, being formed probably from the decomposition of vegetable and animal matter in the soil, nearly as in artificial nitre-beds. It effloresces sometimes on lime-stone rocks, or in lime-stone caves: and is probably formed by the action of carbonate of lime on the oxygen and nitrogen of the atmosphere, promoting their combination so as to form nitric acid, and the lime-stone perhaps affording the potash with which the acid combines. There is accordingly a constant re-production of it. This is the case at the celebrated Nitre Pit at Molfetta in Apulia. It is intermixed with sulphate of lime; and Klaproth found also associated with it a small quantity of an alkaline muriate. It forms thin layers, of a crystalline appearance, of a greyish or yellowish white colour; and is easily distinguished by its cool taste, and by detonating on burning fuel.

CARBONATE OF SODA, or NATRON, is found native under different forms. In some districts in Syria and India, it occurs in efflorescence on the soil. In the kingdom of Tripoli, it is found in crystalline encrustations of the thickness of from one-third to half an inch, exhibiting a striated fracture, being apparently composed of acicular crystals, which are aggregated. This forms what has been named Trona. It was analysed by Klaproth, and was found to consist of 37 of soda, 38 of carbonic acid, 22.5 of water of crystallization, and 2.5 of sulphate of soda. It is therefore partly a bi-carbonate. A variety has been brought from Brazil, in masses having no crystalline structure, which is a perfect bi-carbonate*. This salt also exists in solution in the water of certain lakes, from the borders of which it is often deposited. In Hungary, there are lakes of this kind, and in Egypt it has been procured from this source from the most remote period. In the French expedition to that country, an opportunity was afforded of examining the Natron Lakes. They are situated in a valley surrounded with calcareous rocks; the bottom of the lakes is chalk mixed with sand, and the soil is impregnated with common salt. The water in the lakes contains muriate of soda, carbonate of soda, and a small quantity of sulphate of soda; the borders of the lakes are covered with crystalline masses, and the sides and bottom are encrusted with saline matter. These masses are of a granulated crystalline structure, of a greyish white or light brown colour: in some specimens the natron is nearly pure carbonate of soda, in others mixed with muriate of soda, sulphate of soda, and carbonate of lime: in all of them the carbonate is easily discovered, by effervescing with an acid. Berthollet ascribes its formation, with much probability, to the infiltration of water through the soil, which dissolves the muriate and sulphate of soda, and presents them to the action, under an extensive surface, of

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* Nicholson's Journal, vol. xxxv. p. 48.

carbonate of lime, aided by the efflorescence from the porosity of the soil, and the reeds which grow in it; whence the carbonate of soda, as it is formed, is abstracted from the action of the muriate of lime*. The trona of Tripoli, it is singular, has no contamination of muriate of soda: that of Brazil has.

Sulphate of Soda is a common ingredient in saline mineral springs, and is sometimes deposited on the borders of salt lakes, or is found as an efflorescence on the soil in the neighbourhood; frequently mixed with muriate, and sometimes with carbonate of soda. It occurs loose, in layers, stalactitic, or crystallized; and is easily discovered by the chemical tests, of not effervescing with acids, giving a precipitate with muriate of barytes, and not being precipitated by carbonate of soda.

Muriate of Soda, Rock Salt, is the most important of the native salts, and the one which can be most truly regarded as a mineral production, as it is found in immense quantity in the interior parts of the earth. It is usually in large masses, having a crystalline structure; of a white, grey, or reddish colour; it is translucent; semitransparent, or transparent, with a vitreous lustre. Its fracture is foliated, with a threefold rectangular cleavage, and its fragments are cubical; one variety has a fibrous fracture. Its specific gravity is 2.14. Its taste is purely saline. In general, it is pure muriate of soda, or contains a very small quantity of foreign salts. An analysis of the English Rock Salt gives the following composition,—muriate of soda 96.5, sulphate of lime 1.6, sulphate of soda 1.8, and muriate of magnesia .07. As a mineral production, rock salt is extensively distributed. It is generally in beds, short, and very thick, connected with rocks of secondary formation, and more particularly with gypsum.

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* Memoirs relative to Egypt, p. 253. 304.

lime-stone, and sand-stone. There are immense deposites of it in the east and south of Germany. In Spain it is abundant. There is a large deposite of it in Cheshire. In the other divisions of the globe, it is not less extensively distributed. Salt springs, which are found in many countries, probably always arise from the infiltration of water over beds of rock salt, or rocks in which it is disseminated.

Borate of Soda, Native Borax.—This substance, which affords the Borax of Commerce, appears to occur in different countries in the east of Asia, but is principally obtained from a large lake in the country of Thibet. It is in masses, or disseminated, more generally crystallized, its crystals being hexaedral prisms, often of considerable size. Their colour is greenish or yellowish white, with a semi-transparency, and a vitreous lustre: the fracture is foliated. Its taste is mild; it is soluble in water, and it melts with intumescence before the blowpipe. Klaproth found its composition to be, boracic acid 37, soda 14.5, water 47. According to the account given by Mr Saunders, who visited Thibet, the native Borax, or Tincal, is deposited in the bed of the lake; it is dug in large masses; and although this has been done for a long period, the quantity is not diminished, the cavities made by digging it being soon filled up. It is principally dug from the sides and shallower places, while from the deeper parts rock salt is said to be brought up. The lake, which is of 20 miles circumference, is supplied by no stream, but by springs from the bottom *.

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* Philosophical Transactions, vol. lxxix. p. 97.

SECT. III.

EARTHY SALTS.

THESE salts are soluble, and have a styptic or a bitter taste. They are distinguished by giving a white precipitate with solution of carbonate of soda.

NATIVE ALUM, Sulphate of Alumina and Potash.—This occurs generally as an efflorescence, either in powder, or in crystals often capillary, with a silky lustre, and having all the properties of an artificial salt. It is often associated with sulphate of iron, which communicates a yellowish or green tinge; is usually found in the interstices of certain varieties of disintegrated slate, and appears to be formed by the action of air and water on the earthy matter.

SULPHATE OF MAGNESIA.—This occurs likewise as an efflorescence, sometimes in slender crystals, and appears to be formed by the action of air and moisture on sulphur and magnesia existing in the earthy matter on which it is formed. It is easily distinguished by its bitter taste, and its chemical characters.

SECT. IV.

METALLIC SALTS.

THESE salts are distinguished by their styptic metallic taste. They afford precipitates with hydro-sulphuret of potash, and are reduced partially or entirely before the flame of the blowpipe on charcoal.

SULPHATE OF ZINC.—Native White Vitriol occurs stalactitic or in tuberose pieces, sometimes in acicular crystals, usually connected with the sulphuret of the metal, and probably formed from it by oxygenation by the action of air and humidity. It is distinguished by its solubility, its styptic metallic taste, and the white smoke of oxide of zinc which it gives when heated on charcoal by the flame of the blowpipe.

Sulphate of Iron, Native Green Vitriol.—This salt is often found connected with native sulphuret of iron, from which it is evidently formed by absorption of oxygen from air and water. It occurs massive, stalactitic, and often crystallized; more or less transparent, with vitreous lustre, and of a green colour, but generally superficially encrusted. Its colour distinguishes it, and it is easily discriminated by the chemical tests of the salts of iron.

Sulphate of Copper, Native Blue Vitriol, occurs in connection with copper pyrites, from which it is evidently formed by oxygenation. It is stalactitic or crystallized; its crystals are of a blue colour, and more or less transparent. The colour, solubility, and deposite of copper, which an iron wire immersed in its solution gives, easily distinguish it.

Sulphate of Cobalt is sometimes found with cobalt ores, though of rare occurrence, and evidently of recent formation. It is stalactitic or in layers, of a reddish colour, is soluble in water, and might be easily distinguished by its solution, with the addition of a little muriate of soda, giving a green colour on paper when heated, and by its giving to borax before the blowpipe a deep blue tinge.

CHAP. II.

EARTHY MINERALS.

Under this order are comprised the fossils formed by the combinations of the earths with each other, or with certain acids. The fixed alkalis enter into the composition of some of these compounds, as do also several of the metallic oxides in smaller proportion. The order is subdivided into genera; each earth, according to the principles of chemical arrangement, forming a genus, to which are referred those fossils of which it is the principal ingredient, or to which it gives the predominating characters. Scarcely any common properties can be assigned to the Earthy Minerals. They are connected entirely by chemical relations. They have been in general said, however, to be light, or only moderately heavy; of pale colours, destitute of metallic lustre, uninflammable, insipid, and insoluble. They are not reduced before the flame of the blowpipe.

SECT. I.

OF BARYTIC MINERALS.

Under this genus there are only two proper species, the Sulphate, and the Carbonate. They are distinguished from other earthy fossils, by their greater specific gravity.

Sulphate of Barytes, Heavy Spar.—The most common variety is the Foliated, so named from its fracture: it occurs massive, and often crystallized: the forms of its crystals are the oblique four-sided prism, and the rectangular four-sided table; perfect, or modified by truncation or bevellment of the edges or angles. The colour is white, with shades of grey, yellow, or red: the lustre shining and vitreous: the crystals are often transparent; the massive often only translucent: the fracture gives a threefold cleavage; the fragments approach to the rhomboidal form: it is easily scratched by the knife: is brittle and heavy, the specific gravity being from 4.3 to 4.5. It melts before the blowpipe into a white enamel, which, when moistened, gives an odour of sulphuretted hydrogen, from the sulphate having been decomposed by the carbonaceous matter of the flame. It consists of 67 of barytes, and 33 of acid; and sometimes contains small proportions of sulphate of strontites, silica, alumina, and iron.

There are other varieties. One has a curved foliated fracture, which passes into splintery. Another, named Granular Heavy Spar, presents a fracture very fine foliated: it contains, according to Klaproth, 0.10 of silica. Compact Heavy Spar has a fracture fine grained uneven, passing into coarse earthy; is massive, has little lustre; opaque, or only translucent on the edges; sometimes the induration is so inconsiderable, as to form an earthy variety. Columnar Heavy Spar derives its name from the appearance of its crystallized masses, which are composed of oblique four-sided prisms, aggregated in a columnar form. Bolognian Heavy Spar occurs in rounded masses, and presents a radiated fracture: the rays, or narrow planes, being parallel or divergent: is translucent; its internal lustre shining and resinous.

Carbonate of Barytes, Witherite of Werner, occurs in veins, massive, in globular pieces, and sometimes though rarely crystallized. Its crystals are six-sided, and double six-sided pyramids: colour white, with a shade of yellowish grey: it is translucent, or semi-transparent; its lustre is shining, and approaching to resinous: its fracture in one direction radiated, in another uneven: its fragments are wedge-shaped: is semi-hard: its specific gravity 4.3. It is fused by the flame of the blowpipe into a white enamel: dissolves with effervescence in diluted nitric acid. According to Withering, it consists of barytes 78.6, carbonic acid 20.8; Klaproth, barytes 78, and carbonic acid 22; and Vauquelin, barytes 74.5, carbonic acid 25.5. Klaproth also found in it about 1.7 of carbonate of strontites in 100 parts. It is found principally in Lancashire, and in Cumberland.

SECT. II.

OF STRONTITIC MINERALS.

The natural species of this genus are those in which the earth is mineralized by sulphuric and by carbonic acids.

The Sulphate occurs massive, and crystallized in six-sided tables, or in rhomboidal four-sided prisms acuminated by four planes. Colour milk-white, frequently with a shade of blue, which deepens into sky-blue; whence the name of Cælestine given to it; in one variety grey, or sometimes of a reddish tinge. The crystals are semi-transparent, or translucent: their lustre more or less shining: the fracture is foliated, fibrous, or compact fine splintery; the specific gravity from 3.5 to 3.8. Consists of strontites 58.25, sulphuric acid 41.75, with a little oxide of iron. Vauquelin found in the compact variety 8 or 10 of carbonate of lime, and a little oxide of iron.

The Carbonate, Strontianite, was first discovered at Strontian in Argyleshire, and has since been found in Saxony. It is usually massive: sometimes shooting into slender crystals, which appear to be six-sided prisms, acuminated by six planes. Colour is light green: sometimes only greenish white or yellowish; is more or less translucent; lustre shining and pearly; fracture fibrous or radiated; the fibres being straight, and generally diverging: is semi-hard, brittle; specific gravity 3.6 or 3.7. Before the flame of the blowpipe, becomes white and opaque, but is not fused. With soda or borax melts into a vitreous enamel. Dissolves in diluted nitric acid with effervescence. According to Dr Hope's analysis of it, it consists of strontites 61.21, carbonic acid 30.2, water 8.59, with which Pelletier's coincides. Klaproth states the proportions at 69.5 of the earth, 30 of acid, and 0.5 of water; and Stroymeyer lately fixed them at 70.3, and 29.7, with about 2 *per cent.* of carbonate of lime.

Bary-Strontianite, or Stromnite.—This name has been given by Dr Traill to a mineral which he discovered in a Lead Mine nigh Stromness in Orkney, and which consists chiefly of carbonate of strontites. It occurs in masses, having some appearance of disintegration; of a greyish or yellowish white colour; the lustre weakly shining and pearly; translucent at the edges. The principal fracture is radiated, the cross fracture uneven; it is brittle and soft; its specific gravity is 3.7. It does not melt before the flame of the blowpipe. Effervesces in acids, especially when diluted, and is partially dissolved. By a careful analysis, Dr Traill found that it is composed of carbonate of strontites 68.6, sulphate of barytes 27.5, carbonate of lime 2.6, oxide of iron 0.1. Whether the carbonate and sulphate are chemically combined, or only in a state of mixture, is uncertain.

SECT. III.

OF CALCAREOUS MINERALS.

The fossils which belong to the calcareous genus consist of lime, combined with different acids. As there is no ambiguity in their composition, their arrangement on chemical principles can be established with precision.

Sulphate of Lime, the first species, named by Mineralogists Gypsum, and, when crystallized, Selenite, occurs under four varieties,—the Earthy, Compact, Fibrous, and Foliated.

Earthy Gypsum is pulverulent, or slightly indurated; of a yellowish or greyish colour; dull, and meagre to the touch: it probably originates in the disintegration of the other varieties.

Compact Gypsum is massive; its fracture is even; sometimes scaly: its colours are shades of grey, often intermixed: has little lustre, but acquires it when polished: is translucent on the edges, and very soft: its specific gravity is from 1.8 to 2.2. It is the substance properly named Alabaster.

Fibrous Gypsum occurs massive: its fracture is fibrous, the fibres being straight or curved, and parallel; its usual colour white, frequently with shades of grey, yellow, or red; its lustre is shining and silky; it is translucent or semi-transparent; is so soft as to be scratched by the nail: its specific gravity 2.3.

The Foliated Gypsum, including the Selenite, occurs both massive and crystallized; the forms of its crystals are the oblique six-sided prism bevelled, or acuminated by four planes at each extremity, and often united, so as to form a twin crystal; the prism sometimes terminates in spherical convex planes; and sometimes these planes united form a spherical convex lens. The colour is generally white, with frequently the shades which the other varieties present: its lustre, when crystallized, is shining, and generally pearly, and it is transparent; when massive the lustre and transparency are less: the fracture is curved and foliated, with a single cleavage; sometimes diverging radiated: that of selenite is large and perfect foliated, generally straight, with a threefold cleavage: it is soft, so as to be scratched by the nail; feels smooth; specific gravity 2.3.

All these varieties have nearly the same chemical characters. Heated before the flame of the blowpipe, they lose their transparency, and become white: when strongly urged by the flame, they give a white or yellowish enamel; the acid being partially decomposed. They do not effervesce with acids, or only slightly from intermixture of carbonate of lime: they are soluble in sulphuric acid, when its action is aided by heat. The purest variety selenite; according to Bergman, consists of lime 32, sulphuric acid 46, water 22: according to Bucholz, of lime 33.9, acid 43.9, water 21; the different varieties frequently contain carbonate of lime, oxide of iron, and silica.

ANHYDROUS SULPHATE OF LIME, or Anhydrite, containing no water in its composition, must be considered as a distinct species from the former. It occurs massive, as well as crystallized; the crystallized variety forming what is called cube spar; the forms of the crystals being a rectangular four-sided prism; sometimes truncated on the lateral edges, so as to form a prism of eight sides: their external lustre is shining and pearly; they are more or less transparent; their colours white, grey, bluish, or flesh-red: the massive presents nearly the same lustre. The hardness is greater than that of the common gypsum; the fracture imperfectly curved foliated: one variety is compact with less lustre; another fibrous; the specific gravity 2.9, considerably above the other species. It is phosphorescent when heated, and is fusible by the blowpipe, without ebullition, into an opaque glass. According to Mr Chenevix's analysis, consists of 44.88 of acid, and 55.12 of lime. According to Klaproth, 42 and 57. It often contains a little muriate of soda, being found naturally associated with rock salt: frequently also with an intermixture of siliceous earth.

What has been called Glanberite, and which occurs crystallized in oblique four-sided prisms, transparent and shining, is composed of sulphate of lime, with sulphate of soda, both free from water.

Carbonate of Lime.—This occurs in very different states, arising from differences in its aggregation, and from the intermixture of other substances. There is hence considerable difficulty in arranging its varieties, and in determining whether some of them ought not even to be regarded as distinct species.

Crystallized Carbonate of Lime, or what has been named Calcareous Spar, is the species in its purest state, or consisting only of lime and carbonic acid. When it occurs amorphous, or of irregular forms, it presents the crystalline structure; more generally it is crystallized. The primary forms of its crystals are the six-sided pyramid, the three-sided pyramid, and the six-sided prism; but these undergo numerous modifications from acumination, bevellment, and truncation, giving rise to a variety of forms: the crystals are generally transparent, or semi-transparent: in its amorphous state, it varies from transparent to translucent: it has very distinctly the property of double refraction: the external lustre is shining and resplendent, and is vitreous: the usual colour is white, but other colours occur, as grey, green, red, yellow, and light purple. The fracture of calcareous spar, in all its forms, is perfectly foliated, with a threefold cleavage: its fragments are rhomboidal: it is semi-hard, so as to be easily scratched by the knife: it is also brittle; its specific gravity is 2.7. It decrepitates before the flame of the blowpipe, but is perfectly infusible. Some varieties are phosphorescent when laid on burning fuel: by a full red heat it is decomposed, its carbonic acid being expelled: it effervesces strongly with the acids, and is entirely soluble in diluted nitric or muriatic acid. It consists of 56 of lime, and 43.5 of carbonic acid, (Vauquelin).

There are some fossils composed principally of carbonate of lime, which appear to differ from it principally in the state of aggregation. Such is the Slate Spar. It occurs massive; has a high pearly lustre; is translucent, and of a white colour, with shades of green or red: its fracture is curved foliated, approaching to slaty, with a single cleavage: its fragments are slaty, or wedge-shaped; is soft, so as to be scratched by the nail: its specific gravity is 2.7. It effervesces strongly with acids. It has been analysed by Mr Aikin, who has stated its composition at—carbonate of lime 98.118, silex 0.5, oxide of iron .8, with 1.032 of loss. This fossil appears to pass into what has been named Aphrite, Schaum Earth, or Silvery Chalk; which has the same pearly lustre and colours, and a fracture curved foliated, but occurs in a less state of induration, being so soft as to soil, and sometimes being composed of fine scaly particles nearly loose. Nor does what has been named Schaalstone appear to be essentially different: like the preceding, it occurs massive; is of a white colour, with shades of green, red, or yellow, and a lustre shining and pearly. Its fracture is foliated, with a single cleavage: it is translucent and semi-hard. It has been supposed to consist of carbonate of lime, with a portion of silica.

Fibrous Carbonate of Lime.—This variety, distinguished by its fibrous texture, occurs massive, or in various imitative shapes; the stalactites and stalagmites, which are deposited from water, holding carbonate of lime in solution, belong to it, but it also occurs, not of stalactitic origin, in veins. This latter variety is in its fracture distinctly fibrous; the fibres being straight and parallel; its colour is white, with shades of grey, yellow, or red; its lustre is shining and pearly; it is translucent; is semi-hard, and gives splintery fragments. Its chemical characters are the same with those of calcareous spar, and its composition is similar.

The Stalactitic Carbonate, the other variety of the fibrous kind, is, from the nature of its formation, presented under various external shapes, conical, tuberose, coraliform, and botryoidal. Its colour is white, with shades of grey, yellow, red, and green; its lustre is weakly shining; it is translucent, approaching to semi-transparent; its fracture is fibrous; the fibres being generally divergent; it is rather softer than calcareous spar: its specific gravity is 2.7. Its chemical characters are the same with those of the other varieties of carbonate of lime. The Pisolithe, or Peastone, so named from the mass being composed of small rounded concretions like peas, which consist of carbonate of lime, appears to be of similar origin. Roestone is probably connected with this. It is in mass composed of small globular concretions, dull, opaque, of a brown or yellowish colour, soft, and easily broken.

Granular Carbonate of Lime, or Granular Limestone.—This occurs in extensive strata, generally connected with primitive rocks, or those of transition; and hence sometimes receiving the name of Primitive Limestone. In its structure, it shews indications of a crystalline arrangement; its fracture is small foliated, sometimes splintery, and presents granular distinct concretions: its usual colours are white and grey; its lustre varies from shining to glimmering, and is intermediate between pearly and vitreous; it is translucent; is semi-hard, rather harder than calcareous spar, and less brittle. Its specific gravity is 2.7 or 2.8. It effervesces with acids; and is dissolved, leaving more or less residue. The analysis of few of its varieties has been accurately executed. It appears often to be a carbonate of lime nearly pure, but it also contains silica, alumina, and magnesia, in proportions variable, and not well determined. I have found it to lose by dissolving in muriatic acid 0.42 of weight, which is nearly the same that calcareous spar loses. In Carrara marble, which is one of the purest of this family, Kirwan found only 0.03 of alumina, with 45 of carbonic acid.

The granular limestone furnishes some of the finest marbles, particularly those which are used for statuary.

COMPACT CARBONATE OF LIME, or Compact Limestone.—In this fossil, common limestone, the carbonate of lime is much less pure, and hence it wants the characters which belong to the purer varieties. Its fracture is compact, generally small scaly, passing into large conchoidal, uneven or earthy. Its usual colour is grey, but frequently diversified with shades of other colours: it is dull, and a little translucid on the edges: it is semi-hard, passing to soft; has a specific gravity of 2.6 or 2.7. It occurs stratified, in connection with the secondary strata: it often contains the remains and impressions of organic beings, particularly of marine animals. Its composition varies considerably: the base is carbonate of lime, but with this are intermixed, in the several varieties, variable and often considerable proportions of alumina, silica, magnesia, and oxide of iron. In burning into lime, they lose from 25 to 35 of their weight, and by solution in acids, sometimes do not lose more than 0.22.

Lucullite, or Fœtid carbonate of lime, is, according to Vauquelin, a carbonate impregnated with sulphuretted hydrogen, from which it derives an unpleasant odour, perceptible when rubbed; it also contains a little bituminous carbonaceous matter. It occurs massive in beds: its colour is brown or black, with little lustre; is opaque; its fracture is earthy, inclining often to slaty. When heated, it loses its colour and smell, and is converted into lime.

EARTHY CARBONATE OF LIME includes Chalk and

Marl. Chalk is carbonate of lime in a state of loose aggregation, having usually intermixed small portions of silica and alumina, with a little oxide of iron. It occurs massive, generally in beds: its fracture is earthy: its colour white, or yellowish, dull, and opaque; is so soft as to soil; its specific gravity is 2.3. It dissolves readily in acids with considerable effervescence.

Marl is an impure carbonate in a loose state of aggregation. There are two varieties,—the earthy and indurated; the former is composed of earthy particles, is dull, and feels meagre: the other is more indurated, but is still so soft as to yield to the nail; has an earthy fracture; is dull and opaque; effervesces with acids, and generally falls to powder in water, or under exposure to atmospheric air. Marls contain, besides carbonate of lime, generally clay in largest proportion, and, next to this, magnesia, silica, and oxide of iron, in variable quantities.

The Bituminous Marl Slate is more highly indurated, and has a slaty fracture. It occurs stratified, and is distinguished by frequently having impressions of fish.

There remain some fossils, in which carbonate of lime is so modified, or is chemically combined with other principles, so as to constitute distinct species.

The one in which the quantity of foreign matter is least considerable, is the fossil which has been named Arragon Spar, or Arragonite. Hauy, in subjecting it to crystallographical examination, found that the cleavage was different from that of calcareous spar, indicating a different crystalline arrangement, and a difference in the forms of their primitive molecules; they differ also in hardness and specific gravity. It occurs crystallized in hexaedral prisms, either perfect, or bevelled at the extremities: its colour is white: its lustre shining and vitreous; it varies from transparent to translucent, and gives a double image: its fracture is imperfectly foliated: it is much harder than common calcareous spar, so as to scratch it easily: its specific gravity is greater, being 2.946. It effervesces with acids, decrepitates and calcines without fusion. These differences led repeatedly to its analysis, but it was found only composed of lime and carbonic acid, without any trace of foreign ingredient. This was the result of the analysis executed by Klaproth: the same result was obtained by Thenard. The inquiry was resumed by Fourcroy and Vauquelin, and the identity of the two fossils, with regard to the quantity of lime and carbonic acid which they afforded, appeared to be established, or with differences so trivial as to be inadequate to explain the difference in characters, 100 parts of arragonite affording, by solution in nitric acid, 43 of carbonic acid gas, and, by calcination, 55 of lime; the same quantity of pure calcareous spar from Iceland, giving 43.5 of gas, and 56 of lime [*]. It was resumed by Thenard, with the utmost attention to every circumstance, but still with the same result. The proportions obtained from both were 54.34 of lime, 43.28 of carbonic acid, and 00.38 of water [†]; and in both series of experiments, no difference could be discovered in the presence or absence of water. This fossil, therefore, continued to afford a singular opposition between mineralogical distinctions, and chemical analysis. Stroymeyer at length discovered that it contains a portion of strontites in the state of carbonate: he detected it by dissolving the arragonite in nitric acid, evaporating the solution till it crystallizes, and digesting the crystals in alkohol; the nitrate of strontites remains undissolved. The quantity of carbonate in the arragonite amounts, he found, to between 3 and 4 *per cent.* He justly remarked, that a small quantity of a foreign ingredient is often sufficient to modify the properties of a crystallized body, and as no other cause can be assigned for the peculiarities of the arragonite, it can

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[*] Memoires d'Arcueil, tom. ii. p. 177.

[†] Philosophical Transactions, 1805, p. 325.

scarcely be doubted that it depends on this. Some chemists, Bucholz in particular, have since repeated the analysis, and although they found strontites in some varieties, could not discover it in others. But its detection is difficult, and when in minute quantity, may not be easily attained. Laugier has since found it in very small quantity in some of these varieties in which Bucholz could discover none; and others from which he did not obtain it, had not all the characteristic properties of arragonite; while those which were most distinctly marked, contained the largest proportion. Stroymeyer found also a minute quantity of water chemically combined in the arragonite *.

The hard carbonate of lime described by Bournon †, and which exhibits a similar anomaly, is probably to be placed with the arragonite. Its specific gravity is nearly the same, being 2.912: its hardness is equally superior to that of calcareous spar, and even exceeds a little that of the arragonite itself.

Rhomb Spar, or Bitter Spar, is carbonate of lime, with carbonate of magnesia, and smaller quantities of oxide or carbonate of iron, and of manganese. It occurs in rhombs, usually semi-transparent or translucent, having a shining lustre, vitreous, inclining to pearly; of a white colour, with a shade of yellow or grey. The fracture is straight foliated, with a threefold cleavage; its fragments are rhomboidal; it is harder than calcareous spar, and heavier, the specific gravity being 2.89. It splits before the flame of the blowpipe, and acquires a brown colour. It effervesces with acids only when it is in powder. The proportions of its constituent parts are very various. Klaproth in one variety found 73 of carbonate of lime, 25 carbonate of magnesia, and 2.25 oxides of iron and manganese; in another 68 of the first, and 25 of the second. In one

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* Annals of Philosophy, vol. iv. p. 245. 250. vol. x. p. 151. 387. Annales de Chimie et Physique, tom. ii. p. 176.

† Philosophical Transactions, 1803, p. 325.

which I submitted to a careful analysis, I obtained 56.6 of carbonate of lime, and 42 of carbonate of magnesia, with a trace of manganese and iron.

Dolomite, or Magnesian Limestone, appears to be the same compound in a massive state. It occurs in extensive beds; and is easily distinguished from common limestone, by its effervescing feebly with acids, and dissolving slowly.

Pearl spar, or Brown spar, contains carbonate of iron, and generally carbonate of manganese. It occurs massive, disseminated, and crystallized; its crystals being rhombs, or lenses: its colours are white, often with shades of grey, yellow, or red; but, from exposure to the air, its colour darkens, it becomes brown, and at length nearly black. Its lustre is shining and pearly: it is semi-transparent; when massive, translucent: its fracture is foliated, the lamellæ being more or less curved: it has a triple cleavage: its fragments are rhomboidal: its hardness rather greater than that of calcareous spar: its specific gravity is 2.8. It is blackened before the blowpipe: it effervesces with acids, but not strongly. The composition of this fossil is extremely various. With carbonates of lime, manganese, and iron, it often also contains carbonate of magnesia; the proportions are very different, and sometimes the proportion of carbonate of lime diminishes greatly, that of magnesia increasing: when the metallic carbonates increase, it forms the transition into sparry iron ore. The oxide of manganese appears to be at the minimum of oxidation; and it is from it gradually absorbing oxygen, that the change of colour which pearl spar suffers from exposure to the atmosphere happens.

Phosphate of Lime.—This species occurs under different forms, which can be connected only by their chemical characters. One variety of it, first found in Estramadura in Spain, is found massive in extensive strata; under this form it has been named Phosphorite. It is earthy, or when more indurated has a foliated fracture. Its colour is yellowish white, without lustre or transparency; its specific gravity 2.8. It is distinguished by a high degree of phosphorescence when heated or rubbed: when thrown on burning fuel, it gives a beautiful yellow light. Pelletier found it to consist of lime 59, phosphoric acid 34, fluoric acid 2.5, silica 2, iron 1, with a trace of carbonic and muriatic acids.

The fossil which has received the name of Apatite, is another variety of phosphate of lime. It occurs crystallized; the form of its crystals being the equiangular six-sided prism, or six-sided table: the crystals are small: the colour is white, green, and blue, of various shades, generally pale; their lustre resplendent; they vary from transparent to translucid: the fracture is imperfectly foliated: specific gravity 3.2. On burning fuel, it gives a greenish phosphoric light. It loses colour, but does not melt before the blowpipe. It is soluble in nitric acid. According to Klaproth's analysis, it consists of 55 of lime, and 45 of phosphoric acid.

There is a third variety of phosphate of lime, which has so high a degree of lustre and transparency, as to have been confounded with a different fossil, under the name of Chrysolite. Vauquelin, on analysing it, was surprised to find it composed of phosphoric acid and lime. It occurs crystallized, in equiangular six-sided prisms, acuminated by six planes. Its colour is asparagus-green, whence it has received the name of Asparagus or Spargel Stone: its lustre is shining or resplendent, and resinous: it varies from translucent to nearly transparent; its fracture is foliated: it is semi-hard, brittle; its specific gravity 3. It is soluble in nitric and muriatic acids, without effervescence; but does not, like the other varieties of this species, give any phosphoric light on burning fuel. It is not melted by the blowpipe. The proportions of its constituent parts were found by Vauquelin and Klaproth to be 53.32 of lime, and 45.72 of phosphoric acid.

Fluate of Lime.—This fossil, distinguished generally by the beauty of its colours, occurs under two varieties,—the compact and the foliated; the latter of which is the most common, and is the mineral to which the name of Fluor-Spar is generally given. It is found massive, and often crystallized: the forms of its crystals are the cube, perfect, or modified by truncation of the angles or edges, bevellment of the edges, and acumination of the angles. Its colours are extremely diversified, principally shades of purple, yellow, green, blue, red, and grey, and often intermixed: the lustre is resplendent or shining, and is vitreous: the transparency varies from transparent to translucent: the fracture is foliated, with a fourfold cleavage: it scratches calcareous spar, but is scratched by the knife: it is brittle: its specific gravity is 3.1 or 3.2. Before the flame of the blowpipe it decrepitates, and then melts into an enamel of a greyish white colour. When placed on burning fuel, or on a red hot iron, it gives a beautiful purple light, and is also phosphorescent from friction. Richter stated its composition at 35 of acid, and 65 of lime; Klaproth at 32.25 and 67.75; and Dr Thomson at 32.66 and 67.34.

The variety named Compact Fluor, is distinguished by its fracture, which is even: it has always less lustre than the foliated; and is only translucent.

Siliceous Borate of Lime, Datholite.—This occurs massive and crystallized, in oblique four-sided prisms, having a shining and resinous lustre; of a white colour, with often a shade of green; translucent or transparent; of an uneven fracture; semi-hard; specific gravity 2.98. It melts with intumescence before the blowpipe, into a vitreous globule. Consists, according to Klaproth, of 36.5 of silica, 35 of lime, 24 of boracic acid, and 4 of water. What has been called Botryolite, from occurring in botryoidal shaped masses, is of similar composition, containing only 13.5 *per cent.* of boracic acid.

SECT. IV.

OF MAGNESIAN MINERALS.

UNDER this genus are comprehended, not only those minerals in which magnesia is in largest proportion, but those also in which, though in smaller proportion, there exist certain characters peculiar to the genus. These are softness, and apparent unctuosity; the greater number of the magnesian fossils being possessed of these, and being in general destitute of the hardness, lustre, and transparency, which belong to the siliceous and argillaceous genera. They have also usually a green colour more or less deep.

HYDRATE OF MAGNESIA.—This interesting mineral was discovered by Dr Bruce of New York; he found it to be composed of 70 of magnesia, and 30 of water. It occurs in layers, forming thin veins, in serpentine; is of a white colour, pearly lustre, and transparent in thin folia; of a foliated fracture; soft, and very slightly elastic; specific gravity 2.13. It dissolves entirely in acids, without effervescence.

CARBONATE OF MAGNESIA, Magnesite, appears, from its analysis by Dr Mitchell, to be a carbonate, to consist of magnesia and carbonic acid, in nearly equal parts. It occurs in tuberose pieces, of a yellowish grey colour, without lustre or transparency; it is soft, feels meagre, and adheres a little to the tongue.

SILICEOUS CARBONATE OF MAGNESIA.—This constitutes the substance which has received the name of Meerschaum; the proportions, in one variety analysed by Klaproth, being silica 41, magnesia 18.25, lime 0.5, water and carbonic acid 39. Its colour is yellowish white, with a shade of grey, or red, without lustre: its fracture is earthy, passing into conchoidal: it is soft, feels a little greasy, and adheres to the tongue: its specific gravity is 1.6. It is not melted by the heat of the blowpipe. It is a substance powerfully hygrometric, hence the large quantity of water it contains: the proportion of carbonic acid is often so small, that it does not effervesce with acids, and it is perhaps not originally in the state of carbonate.

BORATE OF MAGNESIA, Boracite.—This fossil is found near Luneburg in Hanover, crystallized in cubes truncated on the angles, which are so hard as to scratch glass; semi-transparent, of a white colour, with shining lustre. They become electric by heat; fuse before the flame of the blowpipe with ebullition; and form a yellow enamel. It is not soluble in acids but with the assistance of heat. An analysis of it by Westrumb, gave as its ingredients, boracic acid 68, lime 11, magnesia 13.5. Vauquelin, however, repeating the analysis on a pure specimen, found only boracic acid and magnesia, in the proportion of 63.4 of the former, and 36.6 of the latter. It has been since found at Segeberg in Holstein, in perfect cubes; and Pfaff finds this variety to be composed, exclusive of a little iron and silica intermixed, of 63.7 of boracic acid, and 36.3 of magnesia.

STEATITE, named also Soap-Stone, from its feeling soapy, occurs massive, disseminated, and also in supposititious crystals. The colour is greyish, greenish, or reddish white: externally it is somewhat shining, as is also the streak; internally it is dull: it is translucent on the edges: its fracture is uneven: it is soft; feels unctuous; does not adhere to the tongue: its specific gravity is 2.6. It does not melt before the blowpipe, but becomes white and very hard. The proportions of its constituent parts vary. One variety analysed by Klaproth, gave silica 48, magnesia 20.5, alumina 14, oxide of iron 1, water 15.5; another, silica 59.5, magnesia 30.5, oxide of iron 2.5, water 5.5.

Potstone is allied to steatite. It occurs massive; is of a grey colour, passing into green, with sometimes a shade of red. Its internal lustre is weakly shining: it is opaque or translucent on the edges. Its fracture is curved foliated, or imperfectly slaty: it is soft; feels unctuous: its specific gravity is 2.8. It is infusible before the blowpipe, and hardens in the fire. According to an analysis of it by Wiegleb, it consists of silica 38.12, magnesia 38.54, alumina 6.66, iron 15.02.

Serpentine derives its name from the variegated disposition of its colours. The principal colour is green, with which are intermixed spots or streaks of red, sometimes yellow, or green of a different shade from that which forms the ground. It has no lustre, though it acquires it when polished; is without transparency, or only faintly translucent on the edges. Its fracture is splintery, or fine grained uneven: it is easily scratched by the knife: its specific gravity is 2.6. It feels soft, but with little unctuosity. It occurs massive, and forms entire rocks. Before the blowpipe it remains infusible. By a strong heat it is hardened, and becomes red. Serpentine seems to consist essentially of silica and magnesia, to which are often added alumina, oxide of iron, and sometimes a minute portion of oxide of chrome.

The precious serpentine has been distinguished from the common as a sub-species: it has more lustre and transparency: its fracture is conchoidal.

The fossil named Schillerstone was considered as a variety of hornblende; it was regarded by Werner as rather allied to serpentine; and from its analysis, this appears to be just. It occurs massive or disseminated, or imbedded in serpentine. Its colour is green, generally dark, with sometimes a shade of yellow: its lustre is shining and semi-metallic; and varies according to the position with regard to incident light: its fracture is foliated: it is soft:

its specific gravity is 2.8. It hardens at a very intense heat, and, when borax is added, is fused before the blowpipe. According to its analysis by Drapier, it consists of silica 41, magnesia 29, alumina 3, lime 1, oxide of iron 14, and 10 of water.

CHLORITE.—This fossil has been placed under the argillaceous class; but the proportion of magnesia it contains is greater, and in its general characters it is allied to the magnesian fossils. There are several varieties of it, according to the state of aggregation. Common Chlorite occurs massive and disseminated; its colour is dark green; its lustre is weakly shining, and it is opaque; its fracture is earthy, or fine foliated: it feels meagre, or very slightly unctuous. According to an analysis by Hœpfner, it consists of 41.5 of silica, 39.4 of magnesia, 6.1 alumina, 1.5 lime, 10 iron, and 1.5 water. Foliated Chlorite, so named from its fracture, occurs massive and crystallized in six-sided tables; its colour is dark green; its lustre shining and pearly, inclining to resinous; it is translucent on the edges; is soft, and feels rather unctuous. It consists, according to Lampadius, of silica 35, magnesia 29.9, alumina 18, oxide of iron 9.7, water 2.7. Chlorite Slate, distinguished by its slaty fracture, forms a mountain rock: its colour is green, with a weak lustre, somewhat resinous. Earthy Chlorite is composed of small scaly particles, with little lustre; of a dark green colour; feels rather greasy; and when breathed on, gives an earthy smell. According to Hœpfner, it consists of magnesia 43.7, silica 37.5, alumina 4.1, lime 1.6, and iron 12.9. What has been named Green Earth, and which occurs often incrusting the agate balls found in amygdaloid, or filling the cavities of the rock, is similar to earthy chlorite.

TALC occurs massive, disseminated, and sometimes in small tabular crystals. Its colour is light green, with frequently a shade of yellow: its lustre is shining, pearly, or sometimes semi-metallic: it is translucent or transparent in thin leaves: its fracture is foliated, straight, or curved: the thin plates into which it is divisible are flexible, but not elastic,—a character by which it is distinguished from mica; it is also unctuous to the touch. It does not melt easily before the blowpipe. It consists, according to its analysis by Klaproth, of silica 62, magnesia 30.5, oxide of iron 2.5, potash 2.75, with 0.5 of loss. What is named Indurated Talc occurs massive; its fracture is slaty; it is less soft than common talc, and has less lustre. Earthy Talc occurs loosely indurated in small scales of a pearly lustre; friable; soiling a little, and feeling rather unctuous. To this probably belongs the *Craie de Briancon*, or French Chalk, which Vauquelin found to be composed of silica 61.25, magnesia 26.25, water 6, alumina 1, oxide of iron 1, lime 0.75.

Asbestos.—Under this species several varieties are arranged. Common Asbestos occurs massive: its colour is green, of various shades, with intermixture of grey: its lustre is weakly shining: its fracture is fibrous or radiated; the fibres being straight or curved: its fragments are long splintery; and its fibres are rigid: it is soft, or semi-hard: its specific gravity is 2.5. It melts, though with difficulty, before the blowpipe. Its essential ingredients are, silica, magnesia, and iron, but they exist in various proportions.

Amianth.—This name is given to asbestos when its texture is more delicate, so that the fibres are easily separated, are fine and flexible. Its lustre is greater, and is pearly or silky; its colour is generally lighter than the asbestos, and sometimes is nearly silvery-white. It is melted with difficulty by the flame of the blowpipe. In composition it appears to differ from asbestos in containing more silica. From an analysis by Chenevix, the results were, silica 59, magnesia 25, lime 9, alumina 3, iron 2, with 1 of loss. It is this substance which was employed by the ancients to form an incombustible cloth to collect the ashes of the dead on the funeral pile.

Ligniform Asbestos, is that variety in which in texture there is some resemblance to wood: its colour also is wood-brown, of various shades.

The name of Mountain Cork has been given to another variety, from its resemblance to cork. It is in flat pieces, of a grey colour, without lustre, and opaque; its fracture is fibrous; the fibres being short, and interwoven; it is soft; feels meagre, and is so light as to float on water. It melts with difficulty before the blowpipe. It consists of silica 56.2, magnesia 26.1, alumina 2, lime 12.7, iron 3. When its texture is more close, and it occurs in thinner pieces, it is named Mountain Leather.

ACTYNOLITE.—Of this species there are three varieties,—the asbestous, the common, and the glassy actynolite. The first, Asbestous Actynolite, connects it with the preceding species. It occurs massive; its fracture is fibrous or radiated; the fibres being generally scopiform divergent: its colour is greenish grey: its lustre shining and silky: it is opaque: is soft: its specific gravity is from 2.5 to 2.9. It melts before the blowpipe into a black or grey scoria.

Common Actynolite occurs massive and crystallized: its colour is green: the external lustre resplendent and vitreous: the fracture is diverging radiated: it scratches glass: is brittle: its specific gravity is from 3 to 3.3. According to Bergman, it is composed of silica 64, magnesia 20, alumina 2.7, lime 9.3, iron 4. It melts before the blowpipe into a blackish scoria.

The third variety is the GLASSY ACTYNOLITE.—It occurs massive, or in acicular crystals: its colour is green, passing into greenish white: its lustre shining and vitreous: its fracture fibrous or radiated: is brittle, and moderately hard: its specific gravity is 2.9. It melts into a glass. Laugier found a well defined specimen of it to consist of 50 of silica, with 19.25 of magnesia, 9 of lime, 11 oxide of iron, 3 oxide of chrome, 5 carbonic acid and water.

Granular Actynolite is of a grass-green colour; its fracture is foliated. It occurs imbedded in compact feldspar. The Diallage of Hauy, and the Smaragdite of Saussure, appear to be the same fossil, with slight differences of characters. Hyperstene, or Labradore Hornblende, which occurs imbedded with Labradore Feldspar, of a yellow or red colour, and semi-metallic lustre, has also been considered by Hauy as a variety of common diallage. They all contain silica, magnesia, and iron, as the chief ingredients. Bronzite, which approaches very closely in characters to Hyperstene, is composed of these alone. The common diallage contains chrome, which connects it with the glassy actynolite. Anthophyllite has similar external characters, its lustre being only less metallic, and its specific gravity less. It contains, with silica and magnesia, a portion of alumina, and less iron.

The Glassy Actynolite forms the connecting link with the next species, the TREMOLITE, which also comprehends three varieties,—the Asbestous, the Common, and the Glassy Tremolite. The first occurs massive, of a fibrous fracture, generally divergent, of a white colour, its lustre weakly shining, and silky; it is soft, and brittle. The second, the Common Tremolite, occurs massive, or crystallized in oblique four-sided prisms. Its colours are generally greyish, reddish, or yellowish white: its lustre shining and pearly: is translucent, or semi-transparent: its fracture is broad radiated: it scratches glass: is brittle, the fragments are sharp: its specific gravity about 3.2. The third variety, the Glassy Tremolite, occurs massive, or crystallized in slender prisms, aggregated: its colours are the same as those of the preceding varieties; its lustre, which is shining, is vitreous, passing to pearly; it is translucent; its fracture is radiated, or fibrous; it is semi-hard, brittle, and harsh to the touch.

The varieties of tremolite are often phosphorescent, so that a moderate heat, or the slightest friction, produces a luminous appearance. They are infusible, or melt with great difficulty before the flame of the blowpipe. They consist of silica, magnesia, and lime, with a portion of carbonic acid and water. The proportions in the common tremolite were found by Laugier to be silica 50, magnesia 25, lime 18, carbonic acid and water 5. In the Glassy Tremolite, he found the lime in larger relative quantity, with an increased proportion of carbonic acid; in one specimen, for example, silica 35.5, lime 26.5, magnesia 16.5, and carbonic acid 23.

SECT. V.

OF ARGILLACEOUS MINERALS.

No common characters can be assigned to the genus of Argillaceous Fossils; the gems distinguished by transparency, lustre, and hardness, being comprised under it equally with the dull and plastic clays. They are connected entirely by their chemical relations, to Alumina, their base.

The gems had been placed among the siliceous fossils, as allied with several of them in external characters, and silica had been supposed to be their principal ingredient. Bergman first shewed the error of this opinion, and proved by analysis, that in the emerald, sapphire, topaz, ruby, and hyacinth, alumina predominates. The specific characters of these fossils had also been perplexed by the distinctions of the jewellers, founded on those qualities which give them mercantile value, and particularly on colour, the most variable of all the external characters; and it has required much mineralogical discussion to establish the proper species. Romé de L'isle first inferred, from the identity of their crystalline forms, that the principal gems, distinguished by the epithet of Oriental, the ruby, sapphire, and topaz, are varieties of one species, to which he gave the name of Oriental Ruby. Werner gave to the species the name of Sapphire; Hauy that of Télésie; and Bournon, from their connection with the fossil named Corundum, has distinguished them by the name of Perfect Corundum. This arrangement has been confirmed by chemical analysis, the experiments of Klaproth, Vauquelin, and Chenevix, having proved that all of them consist of alumina nearly pure.

Perfect Corundum, the Sapphire of Werner, occurs in fragments, and crystallized; the forms of its crystals being the double three-sided pyramid, the single six-sided pyramid, and the six-sided prism, modified by truncations and acuminations. Its colours are blue, green, red, yellow, and yellowish white, of numerous shades. It is transparent: its lustre is highly resplendent and vitreous: the fracture is conchoidal, or imperfectly foliated: the hardness inferior to that of the diamond, but superior to that of other fossils, and not yielding to the file: the specific gravity is from 3.9 to 4.1. The distinctions from colour form the different gems. The red constitutes the oriental ruby; the blue, the sapphire; the yellow, the topaz; the purple, the amethyst; the green, the emerald; the yellowish green, the chrysolite. It is only to be remarked, that there are gems to which several of these names are also given, which are distinguished by the epithet Occidental, which are altogether different.

These fossils are not fusible by the blowpipe, but are said to have been melted by the heat excited by oxygen gas directed on burning charcoal. Mr Children found both the ruby and the sapphire to remain unmelted in the intense heat of his powerful galvanic battery. They are generally phosphorescent from friction. The variety of a blue colour, the Oriental sapphire, analysed by Klaproth, was found to be composed of 98.5 of alumina, 1 of oxide of iron, and 0.5 of lime: it is alumina, therefore, nearly pure. The ruby afforded to Chenevix, 90 of alumina, 7 of silica, and 1.2 of iron.

Imperfect Corundum, or, as it is generally named, Corundum, has been long used in India, from its great hardness, for polishing hard stones. It occurs massive and crystallized; the forms of its crystals being the same as those of the perfect corundum. Its colour is greenish-white: externally it is dull, internally shining and vitreous: the fracture is foliated: the fragments rhomboidal: it is very hard: its specific gravity is 3.7 or 3.8. From the aggregation of this fossil, it is scarcely acted on by any chemical agent; hence Klaproth at one time supposed it to be composed of a new earth; subsequent investigation proved that it consists chiefly of alumina, the proportions being from 84 to 90, with 5 of silica, and from 1 to 7 of oxide of iron.

The fossil known by the name Emery is of the same family. It occurs massive, or disseminated: is of a grey colour, dull and opaque. Its fracture is fine grained uneven: it is nearly as hard as corundum, and is used like it for polishing the metals. According to Tennant, it is composed of 86.5 of alumina, 3 of silica, and 4 of iron.

To a species, distinguished by the name of Spinelle, are referred the gems known by the name of Spinell, and Balass Ruby. It occurs in grains, and octohedral crystals. Its colour is red, a deep crimson red forming the spinell ruby, a pale rose red the balass ruby: its lustre is resplendent and vitreous: its transparency more or less perfect: its fracture is conchoidal, or foliated: it is very hard: its specific gravity is from 3.5 to 3.7. According to Klaproth, it consists of 74.5 of alumina, 15.5 of silica, 3.25 of magnesia, 1.5 oxide of iron, and 0.75 lime. Vauquelin found it to contain chrome. The Ceylanite, or Pleonaste of Hauy, appears to be a variety of spinell.

The Occidental Topaz, which is found principally in Saxony, Siberia, and Brazil, occurs in fragments, or more frequently crystallized; the form of its crystals being the oblique tetraedral prism, variously modified. Its principal colour is yellow: its lustre is resplendent and vitreous: it varies from transparent to translucent: it is very hard: its specific gravity is 3.5. The Saxon Topaz was found by Vauquelin to consist of alumina and silica; and, by a subsequent analysis, he discovered fluoric acid in it, as well as in the Brazilian topaz, and Klaproth found the former to consist of silica 35, alumina 59, fluoric acid 5; the latter of silica 44.5, alumina 47.5, fluoric acid 7. SCHORLITE, Pycnite of Hauy, is allied in composition with Topaz. It occurs massive, or crystallized in long hexaedral prisms, translucent, and having a moderate lustre, of a light yellow colour, passing into green, or greenish white; its cross fracture is foliated; it is moderately hard and brittle. It consists, according to Klaproth, of 49.5 of alumina, 43 of silica, and 4 of fluoric acid; according to Vauquelin of 60 of alumina, 30 of silica, 6 of fluoric acid, and 2 of lime. PYROPHYSALITHE, which occurs massive, of similar characters, is another variety. Berzelius has lately shewn, that its composition, and that of the topaz, is the same, with variations in the proportions only of a few fractional parts, being 57.45 of alumina, 34.24 of silica, and 7.76 of fluoric acid. The schorlite consists of 51 of alumina, 38.43 of silica, and 8.84 of fluoric acid.

CHRYSOBERYL occurs in grains, and crystallized under the forms of the six-sided table, and the double six-sided pyramid. Its colour is pale-green, often exhibiting a milk-white opalescence: its internal lustre is resplendent: it is semi-transparent: its fracture is conchoidal: it is so hard as to scratch glass: its specific gravity is 3.7: Klaproth states its composition at alumina 71.5, silica 18, lime 6, oxide of iron 1.5, with 3 of loss.

CYANITE occurs massive, disseminated, and crystallized; the crystals being oblique flat tetraedral prisms. Its principal colour is blue; but it is also white and grey; its lustre is shining and pearly: it is translucent, or transparent. Its fracture is radiated, or foliated: it is semi-hard: its specific gravity is 3.5. It consists, according to Klaproth, of alumina 55.5, silica 43, oxide of iron 0.5.

LEPIDOLITE occurs massive: the mass is of a purple colour, but presents white scales, of a pearly lustre: it is translucid on the edges: its fracture is small grained uneven; it is soft; its specific gravity is 2.8. It melts before the blowpipe, with intumescence, into a pearly-like matter. Klaproth found it to be composed of silica 54.5, alumina 38.25, oxide of manganese and iron 0.75, potash 4. Vauquelin found the proportion of potash to be so high as 0.18, and Hisinger found it to amount to 0.09.

MICA is an important fossil, from its extensive distribution, as an ingredient in granite, mica slate, and other aggregate rocks. It occurs disseminated, in thin plates, often of a large size, and sometimes crystallized in six-sided tables, and six-sided prisms; its usual colour is grey; the lustre of its plates is resplendent, and metallic; in thin lamellæ it is transparent; its fracture is foliated, and it is very easily split into folia, which are flexible and elastic; it is soft, and feels smooth, but not unctuous; its specific gravity is from 2.7 to 2.9. It melts, though with difficulty, before the blowpipe into an enamel. According to Klaproth's analysis, it consists of silica 47, alumina from 22 to 34, oxide of iron from 4.5 to 15.5, oxide of manganese 1.7, and potash from 8.7 to 14.5.

HORNBLENDE occurs massive, disseminated, and crystallized; its crystals being oblique four-sided prisms. Its colour is black, with frequently a tinge of green; its internal lustre is shining; when of a black colour it is opaque; when green, translucent on the edges. Its fracture is foliated, or broad radiated; its hardness such that it is scratched by the knife; but it cannot be broken but with difficulty. Its specific gravity is from 3.6 to 3.8. Before the blowpipe, it melts into a greyish black glass. Its composition, according to Klaproth's analysis, is silica 42, alumina 12, lime 11, magnesia 2, oxide of iron 30. It occurs as an ingredient of several mountain rocks, particularly siennite and greenstone. Basaltic Hornblende occurs in six-sided prisms, imbedded; their colour is black; their surface smooth; they are opaque; their lustre is resplendent and vitreous. From Klaproth's analysis it appears to contain only half the proportion of iron that is in common hornblende. Hornblende Slate is distinguished by its slaty fracture; it occurs massive, and often in large beds.

Basalt forms a mountain-rock, assuming often a columnar form. Its colour is greyish black; it is nearly without lustre; is opaque, or feebly translucent on the edges; its fracture is uneven; it is hard, so as to be scratched by the knife with difficulty, and it is not easily broken; its specific gravity is from 2.8 to 3. It melts before the blowpipe into an opaque black glass. According to its analysis by Dr Kennedy, it is composed of silica 48, alumina 16, oxide of iron 16, lime 9, soda 4, muriatic acid 1, water and volatile matter 5; with which Klaproth's nearly corresponds.

Clinkstone has its name from the peculiar sound it gives when struck. It occurs massive, forms beds, and sometimes assumes the columnar form; its colour is grey; it is dull, and translucent on the edges. Its fracture is slaty; it is semi-hard; easily broken; has a specific gravity of 2.5. According to Klaproth's analysis of it, it is composed of silica 57.25, alumina 23.5, oxide of iron 2.25, manganese 0.25, soda 8.10, and water 3.

Wacké is connected with basalt and clinkstone, and forms a transition from them to clay. Its colour is greenish grey, with shades of brown or red; it has scarcely any lustre, and is opaque: its fracture is even; it is soft, easily broken, and is very liable to fall into pieces from exposure to the air. It occurs in large beds, and is often amygdaloidal.

Argillaceous Slate, or Clay Slate, forms extensive strata in connection with other primitive rocks, and likewise with those of transition. Its colour is grey, with various shades of blue, purple, and green; its lustre is weakly shining, or dull; it is opaque; its fracture is slaty, and is often divisible into large tabular masses or plates; its specific gravity is from 2.6 to 2.8. It melts before the blowpipe. Its composition, as found by Kirwan, is silica 38, alumina 26, magnesia 8, lime 14, oxide of iron 14. In some varieties potash has been discovered.

Other kinds of slate have been distinguished, with regard to which it may be doubted if they form proper chemical species; they pass into each other, and the limits of the divisions cannot always be accurately marked. Whetslate, or Hone-stone, is distinguished by its fracture, which is splintery, or scaly. Drawing-Slate is of a greyish black colour, dull, opaque, and soft, so as to write and soil: it contains carbonaceous matter. Alum Slate is distinguished by affording alum from exposure to the air; it must therefore contain potash and sulphur; the last is generally in the state of sulphuret of iron. Bituminous Shale is of a brownish black colour, with little lustre; is very soft: laid on burning fuel, it gives a weak flame and a black smoke; and appears to consist of clay with bitumen. Slate Clay forms the transition into common clay; its fracture is slaty, approaching to earthy; it is opaque and dull: soft, feels meagre, and adheres to the tongue; it softens and breaks down in water.

The term Clay is ambiguous, but is applied to those earthy mixtures more or less indurated, which imbibe water, and may be kneaded into a paste somewhat ductile. Alumina is the base of all of them, and gives this predominating character; it is mixed with various proportions of silica, magnesia, lime, and oxide of iron, the mixture being often mechanical, and giving rise to different varieties not easily accurately marked. Indurated Clay, or Clay-stone, is clay in the highest state of induration. Its fracture is earthy, passing into even or slaty; it is soft, but is not easily diffused in water, and does not form with it a ductile paste; it is dull and opaque. The purest clay is that named Porcelain Clay, from the use to which it is applied; it occurs loosely indurated and earthy; its colour is white, with shades of grey, yellow, and red, without lustre or transparency; it feels soft; in water it falls to powder, and when kneaded forms a ductile paste. It is, in general, infusible by any heat that can be raised. It consists essentially of silica and alumina; but the proportions of these vary considerably. Mr Wedgwood found the porcelain clay of Cornwall to be composed of 60 of alumina, with 20 of silica; in others the silica is in larger proportion. Potter's Clay occurs massive; its fracture is earthy; it is opaque, dull; generally of a yellowish or greyish white colour; it soils, feels soft; adheres to the tongue; is diffusible in water, and forms with it a ductile paste. Klaproth found it composed of 63 of silica, and 37 of alumina. Pipe-clay is a variety of this. Loam is the same substance, mixed with sand, oxide of iron, and various other foreign and accidental substances. The Boles, which are of a red or yellow colour, are of similar composition, and appear to owe their colours to oxide of iron. They are distinguished by their conchoidal fracture. The Ochres are similar to the boles, containing only more oxide of iron. Lithomarge is distinguished by its greater fineness, being composed of scaly particles, with a surface more or less smooth and shining; it is soft, feels greasy, and adheres to the tongue. Fuller's Earth occurs massive, but little indurated; its fracture is earthy, sometimes uneven or slaty; without lustre or transparency; it is soft, and does not adhere much to the tongue. In water it falls to powder, without forming a ductile paste: and is peculiarly distinguished by its detersive quality. Klaproth has given as its composition, silica 53, alumina 10, magnesia 1.25, oxide of iron 9.75, and water 24. Tripoli is found loose or indurated; its fracture is earthy; it feels harsh and dry; does not adhere to the tongue, nor soil; it moulders in water, but does not form a ductile paste: it consists chiefly of silica, with oxide of iron. It is used for polishing the metals and glass.

The fossil named Wavellite appears to be a hydrate of alumina; a little fluoric acid had been said to exist in it, but, according to Klaproth's analysis, it consists of 71.5 of alumina, 28 of water, and 0.5 of oxide of iron: in some varieties with about 0.05 of silica. It occurs in capillary crystals, or in mammillary protuberances, having a radiated structure, white or greenish, semi-transparent, and of moderate pearly lustre.

Cryolite is a fossil which, from its composition, might be regarded as of a saline nature. It consists of alumina with soda, combined with a large quantity of fluoric acid. It has, however, no solubility in water, and is quite insipid. It occurs massive, is of a white colour, with not much lustre, and only translucent. Its fracture is foliated; it is soft and brittle; its specific gravity is 2.9. It melts before the blowpipe with the greatest facility, and then hardens. It dissolves in sulphuric acid, fluoric acid gas being disengaged. Klaproth found it to consist of fluoric acid and water 40.5, soda 36, and alumina 23.5.

SECT. VI.

GLUCINE MINERALS.

The earth which is the base of this genus, was discovered in consequence of the chemical analysis suggested by the identity of crystalline form in the two principal minerals which belong to it, the Emerald and Beryl, and though silica is the ingredient they contain in largest proportion, there can be no doubt but that glucine impresses the predominating character.

The Occidental Emerald forms the species to which the name Emerald is properly applied, the oriental being a variety of corundum. It occurs crystallized, in short six-sided equiangular prisms, perfect or truncated on the edges, lateral or terminal, or on the terminal angles. Its colour is that pure and rich green, which has received from it the name of emerald green: its lustre is resplendent and vitreous; and it varies from translucent to transparent: its fracture is small conchoidal: it is hard, but not much more so than quartz; its specific gravity is 2.6 or 2.7. It is melted, though with difficulty, by the blowpipe into a white glass. Vauquelin found it to be composed of silica 64.5, alumina 16, glucine 13, oxide of chrome 3.25, lime 1.6, water 2.

Beryl is so analogous in properties and composition to the emerald, that it may be doubted if they are not varieties of the same species; chrome only is wanting in the composition of the beryl; to which may be ascribed the absence of the rich green colour of the emerald. Its colour is pale green, which passes into blue or yellow. It occurs in crystals of the same forms as the emerald: their lustre is shining and vitreous; and they are usually transparent: the fracture is imperfectly conchoidal: the hardness superior to that of quartz: the specific gravity 2.7. The beryl is melted with difficulty before the blowpipe. According to Vauquelin's analysis, it is composed of silica 68, alumina 15, glucine 14, lime 2, and oxide of iron 1.

With these species, the fossil named Euclase is connected, its composition being similar to that of beryl; its analysis, according to Vauquelin, affording silica 36, alumina 19, glucine 15, iron 3, with 27 of loss. It occurs crystallized in six-sided prisms: its colour is green; its lustre resplendent and vitreous: it is transparent: the fracture is foliated, with much brittleness; the specific gravity 3.0. It loses its transparency before the blowpipe, and melts into a white enamel.

SECT. VII.

SILICEOUS MINERALS.

The siliceous minerals can scarcely be distinguished by any common characters: for although many of them are possessed of great lustre, transparency, and hardness, these qualities are not possessed by all of them, and are possessed in an equal degree by fossils belonging to other genera.

Quartz, named also, when perfectly transparent, Rock Crystal, may be placed at the head of the genus, as consisting almost entirely of silica. Analysed by Bergman, it was found to be composed of 93 of silica, 6 of alumina, and 1 of oxide of iron; and Rock Crystal was found by Bucholz to consist of silica, with a mere trace of alumina and iron. It occurs crystallized: the usual form of its crystals being the six-sided prism, acuminated by six planes; sometimes the prism is wanting, or nearly so, and then the form is the double six-sided pyramid; and frequently the single six-sided pyramid only is apparent. It occurs also often massive, disseminated, and of various external shapes. Its common colour is white, often with shades of other colours: it also occurs brown, and more rarely yellow and red. Its lustre is highly vitreous: it is transparent, semi-transparent, or sometimes only translucent. Its fracture is splintery, or conchoidal: its fragments are sharp-edged: it is hard, so as to give sparks with steel, and not to be scratched by the knife: its specific gravity is 2.6. It is infusible before the blowpipe; and is even imperfectly softened by the heat excited by a stream of oxygen gas directed on the flame. It is often phosphorescent, so that when two pieces are rubbed together, they emit considerable light. It is a fossil extremely abundant. The transparent crystallized variety occurs generally in veins or drusy cavities: common quartz often constitutes veins, sometimes even entire rocks, and exists abundantly as a constituent part of some of the most important fossil aggregates,—granite, gneiss, mica slate, and others.

Quartz of a purple colour has received the name of AMETHYST: this variety is also distinguished by its fracture presenting thick prismatic distinct concretions: and when of this structure, it receives the same name, though it has little or no purple tinge. ROSE QUARTZ, or Milk Quartz, is another variety. Its colour is rose-red, passing into other shades, and sometimes milk-white; it is semi-transparent; its fracture is conchoidal; it occurs massive. PRASE is ranked as a sub-species of quartz, from which it differs little: its colour is leek-green, of various shades, and it generally occurs massive, rarely crystallized.

CHRYSOPRASE is a very pure siliceous fossil, containing, according to Klaproth, in 100 parts, 96.16 of silica, with 0.83 of lime, and 1 of oxide of nickel. Its colour is apple-green, derived probably from the oxide of nickel. It has little lustre; is translucent or semi-transparent; its fracture is even: it is hard: its specific gravity is 3.2. Before the blowpipe it loses its colour and transparency, but does not melt.

Opal is a siliceous fossil not less pure, or is rather a hydrate of silica. In one variety of what is named the Perfect Opal, Klaproth found the composition to be 90 of silica, with 10 of water: in another of the common opal, 94.5 of silica, 5 of water, and 1 of oxide of iron. The perfect opal, as it is named, is distinguished by the beautiful play of colours which it exhibits, varied according to the position. Its proper colour is milk-white: its lustre is resplendent and vitreous: it is translucent; its fracture is conchoidal: it is moderately hard, and easily frangible: its specific gravity is 2.1. Before the blowpipe it becomes opaque, but is not melted. The common opal has the same characters, but does not present the effulgence of colours of the precious opal. The semi-opal has less lustre, and transparency, is more dense, hard, and heavy; it contains a larger proportion of oxide of iron. Wood opal is wood penetrated with the matter of opal: its fracture shews the ligneous texture.

Some varieties of opal, which have lost the water they contain from exposure to the air, and have become opaque, recover their transparency when immersed in water. These have been named Hydrophanes. Hyalite, which occurs disseminated, of a white colour and glassy lustre, appears to be a variety of the common opal; it consists, according to Bucholz, of 92 of silica, 6.33 of water, and a trace of alumina: Menelite, which occurs imbedded in tuberose masses, in adhesive slate, is allied to the semi-opal; its analysis gave to Klaproth nearly the same results. The fossil named Cat's Eye, from its property of reflecting in certain directions a changeable whitish effulgence, is of the same family; its external characters being not only similar, but its composition, as determined by Klaproth, being nearly the same as that of common opal.

Chalcedony is a species which, in characters, has relations with the preceding fossils, and in composition does not differ greatly from them, being composed, according to Bergman, of 84 of silica, and 16 of alumina; according to Guyton, of 86 of silica, 4 of alumina, 1 of lime, and 7.6 of oxide of iron: according to Trommsdorff, it consists even of silica alone. It occurs massive, frequently in nodules, botryoidal, stalactitic, and sometimes in veins. Its colours are white, with shades of blue, purple, grey, and yellow; and these are often arranged in stripes parallel or concentric: it has not much lustre, but is susceptible of a fine polish, from which lustre is acquired: it is semi-transparent or translucid: its fracture is even: it is hard, so as to strike sparks with steel: its specific gravity is 2.6. It is infusible before the blowpipe. CARNELIAN is distinguished as a sub-species, by its colour, which is red of various shades, passing to yellow, its glistening lustre, and its conchoidal fracture. Cacholong is chalcedony of a milk-white colour, with greater lustre. The name of Onyx is given to that variety of chalcedony in which stripes of different colours alternate: when one of these is red, it is named Sardonyx. When chalcedony is stained with dark coloured spots, veins, or arborizations, it forms the Mocho stone. Lastly, to this species may be referred the AGATES, chalcedony being their basis, intermixed with carnelian, jasper, quartz, or flint, in spots, stripes, zones, arborizations, or irregularly blended.

FLINT is a pure siliceous fossil; the silica in its composition amounting to 97 or 98 in 100 parts, with minute traces of alumina, lime, and oxide of iron and water. It occurs in nodules; its colour is grey, which passes into yellow, brown, or black: its internal lustre is weakly shining: it is translucent: its fracture is perfectly conchoidal: its fragments sharp edged: its hardness is such, that it gives copious sparks with steel: its specific gravity is 2.5. It is infusible before the blowpipe, but loses its colour. Flinty Slate approaches to flint in colour, lustre, transparency, hardness, and other characters; but its fracture is slaty, and it occurs in large masses, forming entire beds. The Lydian Stone, or touchstone, by which the purity of gold or silver is tried, is a variety of this fossil, having an even fracture, darker colour, and rather less hard.

HORNSTONE, or PETROSILEX, is allied to these. Its colour is grey, of various shades: it is dull, and only translucent on the edges: its fracture is splintery, in one variety conchoidal; its fragments are sharp edged. Like the preceding fossils, it is infusible before the blowpipe, and, according to Kirwan's analysis, it contains more alumina. Under this species is placed the siliceous petrified wood, or Woodstone as it is named; which is composed of siliceous matter, having the characters of hornstone, introduced by slow infiltration into the substance of wood, while the vegetable matter, by decomposition, has been removed, and the appearance of the ligneous texture, and often its organic form, remain.

JASPER.—In this fossil the proportion of alumina to silica becomes larger: it also contains usually a considerable proportion of oxide of iron. Its colours are very numerous, and generally dark: the most common are shades of red, yellow, and brown: sometimes it is grey or white: its lustre is weakly shining: and it is generally quite opaque: its fracture is conchoidal: it is inferior in hardness to quartz or flint, but still it is not scratched by the knife: its specific gravity is from 2.3 to 2.7. It is infusible before the blowpipe, but in a high heat it loses its colour. Riband Jasper, or Striped Jasper, is distinguished by its colours being arranged in stripes generally straight. Egyptian Pebble, which occurs in nodules, and exhibits various colours or shades of the same colour, generally shades of brown, in concentric stripes or layers, is another variety. Jasper Opal is distinguished by higher lustre and a perfect conchoidal fracture.

HELIOTROPE, or BLOODSTONE, differs little from jasper.

Its colour is green, usually marked with small crimson red spots; its lustre is nearly resinous, and it is translucent on the edges: its fracture is imperfectly large conchoidal, and its fragments are sharp edged. It takes a fine polish. It consists, according to Trommsdorff, of 84 of silica, 7.5 of alumina, and 5 of iron.

PITCHSTONE.—This fossil has received its name from its resinous or pitchy lustre and appearance. It occurs in veins, or forms entire rocks, often of a porphyritic structure. Its usual colour is green, but it is often brown, red, black, or grey: its lustre is shining, and resinous: it is translucent on the edges: its fracture is imperfectly conchoidal, or coarse splintery: it is moderately hard, and very brittle: its specific gravity is from 2.0 to 2.3. It melts before the blowpipe; by which it is distinguished from any varieties, either of opal or jasper. Its analysis by Klaproth gave 73 of silica, 14.5 of alumina, 1 of lime, 1 of oxide of iron, 1.75 of soda, and 8.5 of water. From pitchstone, there is a transition to what has been called Pearlstone, and from that to Pumice, both occurring light and vesicular, with a pearly lustre, soft and brittle, the former being composed, according to Klaproth's analysis, of silica 75.25, alumina 12, oxide of iron 1.6, lime 5, potash 4.5, water 4.5; the latter of silica 77.5, alumina 17.5, oxide of iron 1.75, soda and potash 3.

OBSIDIAN is related to these fossils, being found with pearlstone and pumice, and passing into them. It is of a deep black colour; sometimes grey, or brown: its lustre is highly splendent and vitreous: it is translucent on the edges: its fracture is large conchoidal: its fragments sharp edged: its specific gravity is 2.3. It melts before the blowpipe into an opaque spongy glass. According to Vauquelin, it is composed of silica 78, alumina 10, lime 1, soda 1.6, potash 6, and oxide of iron 1.

FELDSPAR is an important fossil, from its extensive distribution, as a component part of several aggregate rocks. Foliated Feldspar, the common variety, occurs massive, disseminated, and frequently crystallized, the forms of its crystals being the six and four-sided prism, variously modified. Its colours are numerous, principally red, white, and grey: its lustre is shining, intermediate between vitreous and pearly, and is varied, according to the position with regard to incident light: it is more or less translucent: its fracture is foliated, and its fragments are rhomboidal. It scratches glass. Its specific gravity is from 2.2 to 2.5. It melts before the blowpipe into a white glass. Some varieties suffer disintegration from exposure to the air, become earthy, and ultimately pass into porcelain clay. The analysis of this fossil has given very different resnlts. The essential ingredients appear to be silica, alumina, and potash; and in the purest variety of it, the adularia, Vauquelin found the proportions of these to be 64 of silica, 20 of alumina, 14 of potash, and 2 of lime. In other varieties, the proportions are very various, with the addition also of magnesia, oxide of iron, and, as has likewise been affirmed, barytes.

Foliated Feldspar enters into the composition of many of the most important aggregate rocks. Granite consists of it, intermixed with quartz and mica, and the feldspar usually forms the principal part or basis of the granite. Gneiss is the same aggregate, having a slaty texture; and Siennite is characterised by the addition of hornblende. Greenstone is an aggregate of feldspar and hornblende. And the name of Porphyry is appropriated to a rock where grains or crystals of feldspar are imbedded in the mass.

The name of ADULARIA has been given to a variety of foliated feldspar distinguished by a greater degree of lustre, which is pearly, and reflected from the internal plates, so as to give a silvery appearance, and by more transparency, its colour is greenish or yellowish white: its fracture is foliated; and its fragments rhomboidal. It occurs massive, and in crystals of the same forms as those of common feldspar. It melts before the blowpipe into a white glass. Vauquelin found it to be composed of silica 64, alumina 20, lime 2, potash 14. The Moonstone, as it has been named, is an adularia.

Glassy Feldspar occurs in porphyry slate, crystallized in six-sided tables, and four-sided prisms; its colour is grey; its lustre vitreous; its fracture is foliated, and its fragments rhomboidal. The fossils named Meionite and Sommite, are probably varieties of it.

Macle or Chiastolite, was considered by Werner as a variety of foliated feldspar. It occurs imbedded in slate, in tetraedral prisms, which, when viewed at their extremities, appear composed of four lines jointed at acute angles, leaving an intermediate rhomboidal empty space; hence its name of Hollow Spar.

LABRADORE FELDSPAR is distinguished by the property of reflecting in certain positions, as the light falls upon it, very beautiful colours, particularly blue, green, and red, arising probably from refraction of the rays from the separation of its lamellæ, by partial disintegration. Its proper colour is grey: its lustre is shining: its fracture is foliated. According to Kirwan, it is less fusible than common feldspar, yet it is melted by the blowpipe.

COMPACT FELDSPAR differs from the other varieties. It has less lustre and transparency: its fracture is splintery, or very imperfectly foliated: and its fragments are not rhomboidal: its hardness is also inferior. It is allied to the common feldspar, however, by its general relations, and its chemical characters. It forms large masses, is also a constituent of some aggregate rocks, particularly greenstone, and occurs in imbedded crystals in antique porphyry.

Saussurite, a fossil named from the elder Saussure, who first observed it, and considered it as a variety of Jade, approaches closely in characters to compact feldspar, and according to its analysis by the younger Saussure, differs principally in a larger portion of iron. It afforded silica 44, alumina 30, lime 4, oxide of iron 12.5, oxide of manganese 0.05, soda 6, potash 0.25.

Even the real Jade, or NEPHRITIC STONE, approaches to this species in composition and chemical characters. It had, from the greasy polish which it receives, been classed among the magnesian fossils; but analysis has shewn that it contains no magnesia; its composition, as determined by T. Saussure, being silica 53.75, lime 12.75, alumina 1.5, oxide of iron 5, oxide of manganese 2, soda 10.75, potash 8.5, water 2.25. It occurs in rounded masses; its colour is leek green; it is dull; its fracture is splintery; it is hard, and difficult to break; is slightly unctuous to the touch. Before the blowpipe it melts into a white semi-transparent glass.

Bildstein is the same species, or nearly allied to it; it occurs massive; has a splintery fracture; a greasy feel; its colour is greenish grey, with little lustre, and from its tenacity it is applied to the same purposes as the jade. Agalmatholite, brought from China cut into figures, whence the name of Figure-stone given to it, is a variety of Bildstein. Klaproth found its constituent parts to be silica 62, alumina 24, lime 1, oxide of iron 0.5, water 10. Vauquelin found it to contain potash, its ingredients being silica 56, alumina 29, lime 2, iron 1, water 5, potash 7; and the same proportions nearly have been assigned by John. The alkali, Vauquelin supposes, had escaped Klaproth's notice, and he had ascribed the loss to water. The Axe-stone, so named from being used by the natives of the South Sea islands in making hatchets, is probably also a variety of Bildstein, or Jade. Its colour is green; its lustre feebly shining; its fracture is slaty; and it is not easily broken.

Andaluzite, or Hard Spar, has also a relation to feldspar. It occurs in connection with quartz and mica, and is principally distinguished by its greater density and hardness, and its infusibility before the blowpipe. It is massive, or crystallized in rectangular four-sided prisms; is of a flesh red colour; is translucent; is extremely hard; its specific gravity is 3.165.

Spodumene, or Triphane, is a newly discovered mineral, belonging to the Feldspar family. It occurs massive, of a foliated fracture, with a shining pearly lustre; is translucent, hard, breaks easily, and into rhomboidal fragments. It divides before the flame of the blowpipe, into yellow scales, and then melts into a greenish glass. Vauquelin assigned as its composition, silica 64.4, alumina 24.4, lime 3, potash 5, and oxide of iron 2.2. The newly discovered alkali, lithina, is that which exists in spodumene, as has been already stated, and it is not improbable that it is also contained in some of the analogous minerals which have been inferred to contain potash or soda.

Scapolite is another newly discovered mineral, belonging to the same family. It occurs massive and crystallized, and is distinguished into sub-species, according as its fracture is foliated, radiated, or compact. It melts before the blowpipe into a vitreous globule, and disintegrates from exposure to the air. The composition, as found by Laugier, is silica 45, alumina 33, lime 17.6, soda 1.5, potash 0.5, iron and manganese 1.

Fettstein, or Elaolite, distinguished by its resinous lustre, has been considered as a variety of Scapolite, but it differs from it in other characters, and is altogether different in composition, containing only a trace of lime, with 44 of silica, 34 of alumina, and from 16 to 18 of potash, with from 1 to 4 oxide of iron. In this composition, it approaches to the family of the zeolites, and it has accordingly the same chemical characters.

Zeolite was originally distinguished as a species by two chemical characters, that of fusing with intumescence before the blowpipe into a white spongy glass, and dissolving in acids, the solutions being gelatinous. But minerals have been brought under it by one or other of these characters, which differ so much in others, that some of them, there is reason to believe, are distinct species. The fibrous zeolite, the variety to which the name was first applied, occurs massive, in globular pieces, and in capillary crystals: its colour is white, with shades of red, yellow, and green: its lustre is pearly: it is faintly translucent: is semi-hard, brittle, and has a specific gravity not more than 2.2. Needle Zeolite occurs massive, or crystallized in acicular prisms; the fracture is radiated, the lustre shining and vitreous; the crystals are transparent, or semi-transparent; the hardness and brittleness greater than in the fibrous variety. These two form the MESOTYPE of Hauy. The radiated zeolite occurs in mass and in rectangular four-sided prisms, generally broad, and sometimes so thin as to appear as a table; and frequently manipularly aggregated. The usual colour is white, lustre shining and pearly; and it is translucent, or semi-transparent. The fracture is radiated; its hardness is such that it is scratched by the knife; it is brittle, and its specific gravity seldom exceeds 2. The broad radiated passes into the foliated, which occurs under the same forms: its lustre is greater, approaching to splendent, and is pearly: its crystals are semi-transparent, or transparent. These two constitute chiefly the STILBITE of Hauy. Meally zeolite occurs incrusting the others; or sometimes massive; has an earthy fracture; is friable, dull, and opaque. Efflorescent zeolite, or LOMONITE, is probably a variety of this. It occurs massive or crystallized, of a white colour, with a pearly lustre, and transparent, but suffers disintegration so rapidly from the air, that it falls in a short time into fragments and powder, and becomes opaque.

These varieties of zeolite are closely connected; they pass into each other in external characters; have similar chemical properties; the varieties of stilbite, however, do not in general gelatinate with acids. They appear essentially to consist of silica and alumina, with a smaller proportion of lime, and a considerable quantity of water. Vauquelin, for example, found a needle zeolite to be composed of silica 50.24, alumina 29.3, lime 9.46, and water 10. They often also contain potash or soda; and, according to Gehlen's analysis, the essential distinction between the Mesotype and Stilbite, is that the former contains less lime and more alkali, and the latter also more water. When acted on by acids, the lime and alumina are dissolved, while the silica, diffused through the liquid, gives the gelatinous consistence. The intumescence before the blowpipe is owing to the expulsion of the water from the fused matter.

Apophyllite, or Fish-Eye Stone, has the chemical characters of the zeolites, and similar external characters. It is distinguished by a peculiar slight iridescence in its fracture surface, and by the facility with which it exfoliates when heated. The chief distinction in composition, is its containing only a small portion of alumina, and a large proportion of lime.

Chabasite occurs crystallized, usually in oblique rhombs; of a white colour; translucent, or semi-transparent, with vitreous lustre; semi-hard, with an imperfect conchoidal fracture. It is composed of silica 43.3, alumina 22.7, lime 3.3, soda and potash 9.4, water 21.

Cubizite, or Analcime, once known by the name of Cubic Zeolite, occurs crystallized in cubes, perfect, or acuminated on the angles; its colour is white; its lustre vitreous; it is translucent, semi-transparent, or transparent: it is harder and heavier than any variety of zeolite; it fuses before the blowpipe, but does not form a jelly with acids. Consists of silica 58, alumina 18, lime 2, soda 10, water 8.5.

Natrolite belongs to this family. It occurs massive, and, in its fracture, presents straight or diverging fibres:

its colour is light yellow, with little lustre: it is translucent on the edges. It is distinguished by the large quantity of soda it contains. Klaproth found its constituent parts to be silica 48, alumina 24.25, soda 16.5, oxide of iron 1.75, and water 9 parts. Another mineral was analysed by Dr Thomson, of a composition somewhat similar, with still more soda, which probably belongs to the same species. It consists of silica 38.52, alumina 27.48, soda 23.5, lime 2.7, oxide of iron 1, muriatic acid 3, volatile matter and loss 3.8. He named it Sodalite.

PREHNITE occurs massive, and crystallized in prisms or oblique tables, often aggregated. Its colour is green, of various shades: its lustre shining, of various degrees of transparency: its fracture is radiated: it is hard, so as to scratch glass: its specific gravity is from 2.6 to 2.9. It melts before the blowpipe with intumescence, but does not form a jelly with acids. Klaproth found it to be composed of 43.83 of silica, 30.33 of alumina, 18.33 of lime, 5.66 of oxide of iron, and 1.83 of water.

STAUROLITE, or CROSS STONE, derives its name from occurring in twin crystals, (rectangular four-sided prisms), which intersect each other, so that the double crystal has the appearance of a cross. It occurs also in single crystals. Its colour is white: its lustre shining and vitreous: it is translucent, or semi-transparent: its fracture is foliated: it is hard: its specific gravity is 2.3. It melts before the blowpipe. According to Klaproth's analysis, it consists of 40 of silica, 16 of alumina, 18 of barytes, and 15 of water.

LAZULITE.—This fossil, long known by the name of Lapis Lazuli, is of a rich azure-blue colour, with little lustre, and translucent on the edges: massive; of an uneven fracture; with a specific gravity of 2.7. It melts before the blowpipe into a white enamel; and, if previously calcined, is soluble in acids, forming a jelly. Klaproth found it to be composed of 46 of silica, 14.5 of alumina.

28 of carbonate of lime, 6.5 of sulphate of lime, 3 of oxide of iron, and 2 of water. According to Guyton, the sulphur exists in the state of a sulphuret of iron, and on this he supposes its colour to depend. It has been long used in mosaic work; and its powder furnishes the fine pigment known by the name of Ultra-marine.

There are some similar minerals of a blue colour, the distinctions of which are not well determined. AZURITE is of an indigo-blue colour, and is distinguished chiefly by a foliated fracture, and being softer than lapis lazuli. It loses its colour before the flame of the blowpipe, but does not melt. HAUYNE is of a deep sky-blue colour, and vitreous lustre; semi-transparent; it retains its colour before the flame of the blowpipe, and at length melts with difficulty; with the addition of borax it forms a yellow glass: it forms a jelly with acids. According to Gmelin's analysis, it consists of silica 35.5, alumina 18.9, lime 2.6, sulphate of lime 21.7, potash 15.5, oxide of iron 1.2, sulphuretted hydrogen 3.4, water 1.2. BLUE-SPAR is of a pale smalt-blue, nearly opaque, with little lustre; has an imperfect foliated fracture; becomes white before the blowpipe, and with borax melts into a black glass.

GARNET occurs massive, but more frequently crystallized: the form of its crystals being the dodecaedron, with rhomboidal planes, either perfect, or truncated on the edges. The precious garnet, as it is named, is of a red colour, of various shades: the lustre is shining, and vitreous: it varies in transparency, from completely transparent to translucent: its fracture is conchoidal: it is harder than quartz, so as to scratch it: its specific gravity is from 4 to 4.3. The common garnet has often a tint of brown or green: it has less lustre and transparency; its fracture is uneven; and it is inferior in hardness and specific gravity. Both varieties melt before the blowpipe, the common garnet with most facility. They consist of silica and alumina, with a large proportion of oxide of iron, to which the great specific gravity and dark colour is owing. In the precious garnet, Klaproth found 35.7 of silica, 27.3 of alumina, 36 of iron, and 0.25 of manganese; Vauquelin 36 of silica, 23 of alumina, 3 of lime, and 41 of iron.

PYROPE, or Bohemian Garnet, has the general characters of the species, but is perfectly transparent; its colour is dark blood-red; and it occurs not crystallized, but in imbedded grains. It has been ranked as a variety only, but there appears to be an essential distinction of composition. Klaproth found its constituents to be silica 40, alumina 28.5, lime 3.5, magnesia 10, oxide of iron 16.5, and manganese 0.25.

MELANITE, named Black Garnet, from its deep black colour, is crystallized in six-sided prisms, acuminated by three planes, and the edges truncated: its lustre is shining: it is opaque: its specific gravity 3.8. According to Vauquelin, it is composed of silica 35, alumina 6, lime 32, oxides of iron and manganese 25.

CINNAMON STONE had been regarded as a variety of hyacinth, from its resemblance in external characters; and Lampadius gave an analysis, whence it appeared that zircon is an ingredient of it; but Klaproth repeated the analysis, and found no zircon, its composition being silica 38.8, lime 31.25, alumina 21.2, oxide of iron 6.5, and 2.25 of loss. This composition, he observes, approaches to that of Vesuvian; and the external characters of this fossil connect it with the garnet family. It occurs in fragments of a reddish brown colour, more or less transparent, with a resinous lustre; hard; and having an imperfect conchoidal fracture.

GRENATITE, the Staurotide of Hauy, occurs crystallized, in the form of a broad six-sided prism, sometimes bevelled; the crystals are often double, one intersecting another in the form of a cross; they have a dark reddish brown colour; opaque or translucent; hard and brittle: the composition is silica 33, alumina 44, lime 3.8, oxide of iron 13, oxide of manganese 1.

Leucite, a fossil which occurs in lava, and, from the appearance of its crystallization, named White Garnet, is a distinct species. The form of its crystals is the double eight-sided pyramid, acuminated by four planes. Its colour is white: its internal lustre shining and vitreous: the crystals vary from opaque to transparent: its fracture is foliated: its specific gravity is 2.4. It is not fused before the blowpipe. It is the first mineral in which potash was discovered, Klaproth having found it to be composed of 54 of silica, 24 of alumina, and 21 of potash.

Vesuvian is found crystallized, in the stony masses ejected from Vesuvius, in rectangular four-sided prisms, truncated on the edges. Its colour is olive-green, passing into yellow, or brown; its external lustre is splendent and vitreous: it is translucent: it is harder than quartz: its specific gravity is 3.4. It melts before the blowpipe into a yellowish glass. It consists of silica 35.5, lime 33, alumina 22.25, oxide of iron 7.5, oxide of manganese 6.25.

Olivin occurs in grains or rounded pieces, or sometimes crystallized in rectangular four-sided prisms. Its colour is green, of different shades: its lustre is shining and vitreous: it is semi-transparent: its fracture is small conchoidal: it is inferior in hardness to quartz: its specific gravity is 3.2. It can scarcely be melted by the blowpipe without addition: in nitric acid it loses its colour, becoming of a pale green. It consists of silica 49, magnesia 37.5, lime 0.25, oxide of iron 12.5. With this fossil, the Chrysolite has been united by Hauy: in composition they are nearly the same; and in colour, lustre, hardness, fracture, forms of crystallization, and chemical characters, are similar. Augite resembles olivin, and is often found with it. It differs in the form of its crystals, which is a rectangular six-sided prism, bevelled on the extremities; in its colour being a darker green, approaching to black; in being harder and heavier, the specific gravity being from 3.4 to 3.7: its lustre is shining and resinous: it is translucent, or faintly transparent: its fracture is uneven. It fuses with difficulty before the blowpipe: it is composed, according to Vauquelin, of 52 of silica, 13.2 of lime, 3.33 of alumina, 10 of magnesia, 14.66 of oxide of iron, and 2 of oxide of manganese. COCCOLITE has relations to these fossils. It occurs massive, in granular distinct concretions, is of a green colour, with considerable lustre, and translucent. It consists, according to Abilgaard's analysis, of silica 42, alumina 15, lime 13, oxide of iron 8, oxide of manganese 14, water 3 parts.

SAHLITE occurs massive and in prismatic crystals; is of a green colour, with shining and vitreous lustre; translucent; its fracture is foliated; is semi-hard and brittle: melts, though with much difficulty, before the blowpipe: consists of silica 53, magnesia 19, lime 20, alumina 3, oxides of iron and manganese 4.

SCHORL occurs massive, and frequently crystallized, its crystals being three-sided prisms, acuminated by three planes: its colour is black; its lustre vitreous; is generally opaque: its fracture is uneven: its hardness a little inferior to that of quartz: its specific gravity is 3. It melts with ebullition before the blowpipe into a greyish slag. It becomes electric by heat, presenting at one extremity positive, at the other negative electricity. Its analysis by Klaproth gives silica 36.75, alumina 34.5, magnesia 0.25, potash 6, oxide of iron 21.

Tourmalin is nearly allied to schorl; its forms of crystallization are similar; it differs in its colours, which are brown, green, red, and blue, of numerous shades, generally dark, and by its greater lustre and transparency: its fracture is conchoidal: it is harder than quartz: its specific gravity is from 3.0 to 3.6. It becomes electrical like the schorl by a moderate heat: before the blowpipe it fuses into a grey enamel. It consists, according to Vauquelin, of 40 of silica, 39 of alumina, 3.84 of lime, 12.5 of oxide of iron, and 2 of oxide of manganese. The blue tourmalin has been named Indicolite, the red Rubellite, and some have considered these as distinct species.

Pistacite, Epidote, or Thallite, has been ranked as a variety of actynolite; but it forms a different species. According to its analysis by Descostils, it consists of silica 37, alumina 27, lime 14, oxide of iron 17, oxide of manganese 1.5; with which Vauquelin's corresponds,—a composition which does not differ greatly from that of schorl and tourmalin. It is usually crystallized in six-sided, or oblique four-sided prisms: is of a pistachio green colour: the lustre is shining and vitreous: the crystals are more or less transparent: the fracture is radiated: it is hard and brittle. The fossil named Zoisite probably belongs to this species.

Thumerstone, Axinite, or Violet Schorl, occurs crystallized in flat and oblique rhombs. Its colour is clove-brown, which passes into violet, or grey: its lustre is splendent: it varies from transparent to translucent: its fracture is uneven: its specific gravity is 3.2. It melts before the blowpipe, into a greenish glass. According to Vauquelin, it consists of 44 of silica, 18 of alumina, 19 of lime, 14 of oxide of iron, 4 of oxide of manganese.

Lievrite, or Yenite, occurs massive and crystallized in prisms; of a brownish black colour, with resinous lustre, opaque; fracture uneven; semi-hard: specific gravity from 3.8 to 4. It melts before the blowpipe into a black enamel: is soluble in muriatic acid. Consists of silica 28, lime 12, alumina 0.6, oxide of iron 55, oxide of manganese 3.

Besides the preceding fossils, silica is deposited in a stalactitic form from waters, in which it has been in a state of solution, and forms Siliceous Sinter. This occurs in massive pieces; the surface sometimes botryoidal; its fracture is compact or fibrous; it has sometimes scarcely any lustre; in other varieties is opalescent and pearly; is of a greyish white colour; and is only semi-indurated, so as to be easily broken. The deposite from the Geyser fountain, consists, according to Klaproth's analysis, of 98 of silica, 1.5 of alumina, 0.5 of oxide of iron. Siliceous stalactites are sometimes found, having crystals of quartz on their surface.

SECT. VIII.

ZIRCON MINERALS.

To the zircon genus belong the two fossils in which this earth is found, the Zircon and the Hyacinth.

The Zircon or Jargon occurs in rounded or angular grains, and crystallized; its crystals being tetraedral prisms, or octaedrons. Its principal colour is grey, but it has often shades of green, blue, yellow, and brown : its lustre is resplendent and adamantine; it is transparent; its fracture is small conchoidal; it is extremely hard, so as to be scarcely affected by the file: its specific gravity is 4.6 or 4.7. It does not melt before the flame of the blowpipe, but with borax forms a transparent glass. According to Klaproth's analysis, it consists of zircon 68, silica 31.5, oxide of iron 0.5.

The Hyacinth occurs in grains, or crystallized; the form of its crystals being the tetraedral prism, the dodecaedron, or octaedron; its colour is red; its lustre resplendent and resinous; it is transparent, or semi-transparent; its fracture is foliated; it is very hard, scratching quartz; its specific gravity is 4.6. It loses its colour before the flame of the blowpipe, but is not fused: with borax it melts into a transparent glass. According to Klaproth's analysis, it consists of zircon 70, silica 25, oxide of iron 0.5, with 4.5 of loss.

SECT. IX.

ITTRIOUS MINERALS.

GADOLINITE forms the principal species of the genus of which Ittria is the base. It occurs massive and disseminated: its colour is deep black: its internal lustre is resplendent: it is opaque, or feebly translucent: its fracture is conchoidal: its hardness is such that it is not scratched by the knife: its specific gravity is 4.2. It intumesces before the blowpipe, but is not fused: when heated gently it becomes incandescent. With nitric acid it forms a gelatinous solution. According to Klaproth, it consists of ittria 59.75, silica 21.25, oxide of iron 17.5, alumina 0.5, water 0.5. The analyses of it by Ekeberg and Vauquelin give rather less ittria, and more silica and iron. Berzelius has found that it contains oxide of cerium. His analysis gives silica 25.8, ittria 45, oxide of cerium 16.7, oxide of iron 10.26.

There are some other fossils in which ittria is an ingredient, such as the Ittro-tantalite, the Ittro-cerite, and Orthite, but in these the proportions of oxide of tantalum, and of cerium, are larger; and they therefore rather belong to these metallic genera. The orthite, however, is perhaps a variety of gadolinite with intermixture, as its external characters are very similar.

CHAP. III.

METALLIC MINERALS.

Under this order are comprised those native combinations in which metals are alloyed with each other, or are united with other substances, forming what are named Metallic Ores. The substances with which they are most generally combined, are sulphur, oxygen, and several of the acids, particularly the carbonic, more rarely the sulphuric, muriatic, and phosphoric. The individuals under each genus are connected, even in the strictest mineralogical systems, entirely by their relation to the metal which forms its base, and not by any analogies in external properties; the arrangement, therefore, is purely chemical. Metallic minerals retain in general the characteristic metallic qualities, lustre, opacity, and great specific gravity, though to this there are many exceptions. The greater number of them admit of being reduced partially or completely when heated on charcoal before the flame of the blowpipe; and they often exhale a dense smoke.

SECT. I.

NATIVE GOLD.

Native gold occurs pure, or alloyed with portions of other metals, more particularly with silver, copper, and tellurium. Its colour is yellow; its lustre perfectly metallic;

it is soft, highly malleable, and ductile; its fracture is hackly ; its specific gravity is always above 12, and rarely equal to 19. It occurs sometimes, though rarely crystallized ; the forms of the crystals being the cube, the octaedron, and the dodecaedron, with rhomboidal planes; more frequently it is found disseminated, capillary, filiform, in thin plates or spangles, and massive; another form of it is in small grains in the sand of rivers and streams, forming what is named Gold Dust. Besides this variety of pure Native Gold, there is one of a brass yellow colour, generally disseminated, or in small plates, in which the gold appears to be alloyed with silver and a little iron ; and another of a steel grey colour, passing to yellow, in which the proportion of alloy is greater. Native gold is distinguished by being dissolved only by nitro-muriatic acid.

Some minerals have been regarded as ores of gold, though they are not strictly so, as they contain larger quantities of other metals. The principal of these are the two native alloys of tellurium, the graphic gold ore, or graphic silvanite, and the white silvanite, which pass into each other. These consist of from 20 to 27 of gold, with from 45 to 60 of tellurium, 10 of silver, and sometimes a little lead. The alloy is in minute indeterminate crystals of a greyish white colour, generally attached to each other laterally, and dispersed on the surface of the matrix, so as to bear some resemblance to printed letters; hence the name, Graphic Gold Ore. Gold is also found in smaller quantity in some varieties of pyrites, which are hence named Auriferous, in which it is supposed to be merely disseminated without being combined.

SECT. II.

NATIVE PLATINA.

Platina, like gold, exists only in the metallic form, forming what is named Native Platina, found in South America, not in its original mineral state, but usually in the sand of streams, from which it is collected in searching for gold. It is in the form of grains, usually flattened, which have an intermixture of other metallic substances, but pieces have been met with of large size. Its colour is white, approaching to a light steel grey; its lustre metallic and shining. It is semi-hard, perfectly malleable, flexible, and has a specific gravity above 15. It is the least fusible of the native metals, not melting except in a heat such as that excited by a powerful burning mirror, and it is soluble only in nitro-muriatic acid. It is an alloy, as has been already stated, of platina, with iridium, and other metals. In Brazil, it has been found free from all of them, but an intermixture of grains of palladium. And platina has been found at Guadalcanal in Estremadura, without any of the foreign metals contained in the Ore of Peru.

SECT. III.

ORES OF SILVER.

Silver is found native, and mineralized. Native silver has the general qualities of the metal. Its colour is white, though frequently tarnished; its lustre metallic; it is perfectly malleable and ductile, usually flexible; it is soft; its fracture is hackly. It occurs massive, branched, capillary, in thin plates, and crystallized; the crystals being generally small and aggregated.

By an alloy of antimony with silver, characters are acquired sufficiently distinctive to form a species, which has been named Antimonial Silver. It has less external lustre, its colour is tin-white, its fracture is lamellated, and it is brittle. It exhales a white smoke before the flame of the blowpipe. It consists of from 67 to 84 of silver, with from 24 to 16 of antimony. Another native alloy of silver, forming a species, is that named Arsenical Silver. Its colour is tin-white, tarnished, and often approaching to grey. Its external lustre is weakly shining: its fracture is foliated: it is soft and brittle. Before the blowpipe it exhales vapours of arsenic and antimony. It consists of 35 arsenic, 44.25 iron, 12.75 silver, and 7 of antimony.

Silver mineralized by sulphur, forms Vitreous Silver Ore, or Silver Glance; Sulphuretted Silver. Its colour is lead grey, passing to steel grey; its lustre is shining, or glistening, and metallic; its fracture is uneven; it is soft, malleable, and flexible; its specific gravity is about 7.200. It occurs massive, disseminated, of various imitative shapes, as filiform, and in minute crystals. Before the blowpipe its sulphur is dissipated, and its silver remains. It consists of about 84 of silver, with 16 of sulphur.

The name of Red Silver Ore is given to a species, which, from its composition, may be named Sulphuretted Antimonial Silver. Its colour is red, of various shades; its lustre is shining, and metallic or adamantine; when massive, it is opaque; when crystallized, transparent or semitransparent; its fracture is uneven, is soft and brittle; its specific gravity is from 5.56 to 5.59. It occurs massive, dendritic, and minutely crystallized. Heated on charcoal by the blowpipe, it decrepitates, melts, exhales a white vapour, and gives a globule of silver. It consists, according to Vauquelin's analysis, of silver 56.67, antimony 16.1[illegible], sulphur 15.07, and oxygen 12.13, the metals existing probably as oxides, with which the sulphur is combined.

Grey Silver Ore can scarcely be regarded as an ore of silver, since it contains not more than from 9 to 20 parts of silver in 100 parts, while it contains from 40 to 48 of lead, and from 8 to 21 of antimony; with from 12 to 22 of sulphur, and 1 or 2 of iron. It is therefore a mixture, or compound of metallic sulphurets. There are two varieties of it, the light grey, or white silver ore, the colour of which is a light lead grey; its lustre shining and metallic, and which occurs massive or disseminated; and the dark grey silver ore, the colour of which is iron grey, passing to black, without lustre; having an earthy fracture.

Silver mineralized by muriatic acid, forms a well defined species, Horn Silver Ore, as it has been named. Its colour is pearl grey, passing into white or blue; externally, its lustre is shining; it is translucent, gives a shining streak; is soft, so as to be easily cut, is also malleable; its fracture is fine grained uneven, specific gravity about 4.7. It occurs massive, more frequently crystallized; its crystals being acicular, or cubes which are aggregated. Heated by the blowpipe it melts, exhales a disagreeable odour, and gives a globule of silver. Another chemical character of it is, that when breathed on, and rubbed by a piece of iron or zinc, the rubbed surface exhibits a film of reduced silver. It consists of silver 67.75, muriatic acid 21, sulphuric acid 0.25, oxide of iron 6, alumina 1.75, lime 0.25.

SECT. IV.

ORES OF QUICKSILVER.

Native Quicksilver is found in globules, on the surface, or in the crevices of other mercurial ores, or other fossils, retaining the lustre, opacity, and mobility of the metal. Sometimes it has an addition of silver, so as to give a soft or a firm consistence; and when the proportion of silver is large, it occurs in minute octohedral crystals.

Quicksilver in the state of oxide combined with muriatic, and a portion of sulphuric acid, forms the species named Mercurial Horn Ore. This generally occurs in small crystals. Its colour is grey, with a pearly lustre. It is faintly translucent; its fracture is foliated; it is soft and brittle, so as to be easily scraped, or cut with a knife. Before the blowpipe it is volatilized.

Quicksilver mineralized by sulphur, forms Cinnabar, its most abundant ore. Its colour is red, of various shades; its lustre varying from shining to dull. It occurs massive, disseminated, and in small crystals, which are translucent or semi-transparent; when massive, it is opaque. It is brittle and soft. Its specific gravity varies from 6 to 10. Heated by the blowpipe, it is volatilized, with smoke, a blue flame, and an odour of sulphur. It consists, when pure, according to Klaproth's analysis, of 84.5 of quicksilver, and 14.75 of sulphur.

Hepatic Quicksilver Ore occurs massive. Its colour is dark red, with a shade of grey. It has little lustre, and is opaque. Its fracture is even or slaty. It is soft, brittle, and has a specific gravity of from 7 to 9. Klaproth states as its composition, quicksilver 81.8, sulphur 13.7, charcoal 2.3, silica 0.65, alumina 0.55, oxide of copper 0.2. It is probably cinnabar, altered by intermixture.

SECT. V.

ORES OF COPPER.

Copper occurs native, and likewise mineralized, forming several species of ores, in general well defined.

Native Copper has the general properties of the metal. Its colour is red, but frequently tarnished: its lustre metallic; it is flexible, ductile, and malleable; its fracture is hackly. Its specific gravity is from 7.6 to 8.5. It occurs massive, in branched pieces, dendritic, in thin plates, and indistinctly crystallized.

Copper mineralized by oxygen, forms Red Copper Ore. It occurs massive, in plates, disseminated, and crystallized. Its colour is cochineal-red, approaching to carmine-red; its lustre is semi-metallic, or adamantine; it is opaque when massive; transparent, or semi-transparent, when crystallized; it is semi-hard, brittle; its specific gravity is about 3.9. Its fracture is compact, foliated, or fibrous; whence different varieties are formed. It is pure oxide of copper; consisting, according to Chenevix's analysis of it, of 88.5 of copper, and 11.5 of oxygen: according to Klaproth's, of 91 of copper, and 9 of oxygen. The brick-red or tile-red copper ore, which occurs earthy or little indurated, appears to be a mixture of oxide of copper and oxide of iron.

Oxide of copper combined with carbonic acid, appears to form two species, the Blue Carbonate and the Green Carbonate; the differences between which arise from differences of oxidation and of the proportion of carbonic acid, and in part from the combination of water.

The Blue Carbonate is named Mountain Blue, or Azure Copper Ore. One variety is earthy, usually an incrustation, sometimes massive, the colour of which is smalt-blue without lustre. Another variety is indurated; its principal colour is azure-blue; when crystallized, its lustre is shining; when massive, it is dull; the latter is opaque, while the crystals are translucent, or semi-transparent; the forms of its crystals are the rectangular and rhomboidal four-sided prism, acuminated by four planes; they are small and aggregated. This species dissolves in nitrous acid with effervescence. As analysed by Pelletier, its constituent parts are from 66 to 70 of copper, from 8 to 10 of oxygen, from 18 to 20 of carbonic acid, and 2 of water. According to Klaproth's analysis, it consists of 56 of copper, 14 of oxygen, 24 of carbonic acid, and 6 of water.

The Green Carbonate comprises two varieties, Mountain Green and Malachite. The first is massive, but more generally occurs as an incrustation; its colour is verdegris-green, without lustre; its fracture is earthy or small conchoidal; and it is soft and brittle: it effervesces, though slightly, with acids, and appears to consist of oxide or carbonate of copper, with alumina and lime. The other variety, Malachite, occurs massive, disseminated, incrusting, and crystallized in capillary and acicular prismatic crystals; its colour is green; its lustre is silky or pearly; its fracture is striated, the striæ being usually divergent, sometimes compact. This variety effervesces with acids. The fibrous malachite analysed by Klaproth was found to consist of 58 of copper, 18 of oxygen, 12.5 of carbonic acid, and 11.5 of water. It contains therefore more oxygen and more water than the blue carbonate.

Copper mineralized by phosphoric acid forms a rare ore, formerly regarded as malachite, but found by Klaproth to consist of oxide of copper 68.13, phosphoric acid 30.95. It occurs massive, disseminated, in cubic crystals small and grouped, of a green colour, often black on the surface, with vitreous lustre, and opaque: its fracture is fibrous.

The Muriate constitutes another rare species; it occurs in angular grains; also massive, and crystallized in six and in four-sided prisms which are transparent, with considerable lustre; when massive, it is opaque. It dissolves in nitric and muriatic acids without effervescence, and heated with sulphuric acid, exhales muriatic acid. Analysed by Klaproth and Proust, it has given from 70 to 76 of oxide of copper, about 10 of muriatic acid, and from 12 to 16 of water.

Copper occurs mineralized by arsénic acid, forming combinations which differ with regard to proportion, and the presence of water; giving rise to several varieties, which have even been regarded as distinct species. Their composition was established by Chenevix. One variety occurs crystallized, in the form of an obtuse octaedron. Its usual colour is sky-blue; sometimes apple or grass green; it is translucent, shining; is brittle; has a specific gravity of 2.881. It consists of 49 of oxide of copper, 14 of arsénic acid, and not less than 35 of water. A second is crystallized in hexaedral tables, bevelled on the terminal planes; its colour is deep-emerald green, with much lustre and transparency; it is less hard, and less heavy; its specific gravity being only 2.548. It consists of 58 of oxide of copper, 21 of arsénic acid, and 21 of water. A third is crystallized in the form of an acute octaedron, the crystals sometimes being lengthened and capillary; frequently indeterminate; in some specimens appearing as delicate fibres parallel or divergent; and sometimes in layers, flat or mammillated, and of a fibrous texture. The colour in these is dark olive-green, passing into brown or yellow, or greenish white; it is generally transparent, or semi-transparent; the lustre is externally shining; it is harder than the preceding varieties, and is much heavier; the specific gravity being 4.280. It consists of from 50 to 60 of oxide of copper, from 30 to 40 of arsénic acid, with, in some varieties, water amounting to 18 or 20 parts. The last variety occurs crystallized in triedral prisms, generally extremely small; they are of a beautiful bluish green colour, but from decomposition often black; when unaltered, they are transparent. Its specific gravity is 4.280. It consists of 54 oxide of copper, 30 arsénic acid, and 16 water.

Copper, in combination with sulphur, with variable proportions of other metals, forms a series of ores, which pass into each other, and which it is difficult to arrange as distinct species, as it is not easy to determine whether some of them are aggregates or compounds of different metallic sulphurets.

Vitreous Copper Ore, or Copper Glance, appears to be the sulphuret of copper in its purest form; it consists of 78.50 of copper, 18.50 of sulphur, 2.25 of iron, and 0.75 of silica. It occurs massive, disseminated, and crystallized, the forms of its crystals being numerous and often imperfect. Its colour is grey; its lustre metallic; its fracture is conchoidal, even, or foliated; its specific gravity is from 4 to 5.3.

In the Purple or Variegated Copper Ore, the proportion of iron is larger, and either it or the copper appears to be slightly oxidated. Klaproth's analysis gave of copper 69.5, of iron 17.5, of sulphur 19, and of oxygen 4 or 5. The colour of a fresh fracture is reddish brown, but it quickly tarnishes; various tints of purple, blue, red, reddish yellow, and green, being assumed and intermixed on the same surface. It occurs usually massive, sometimes disseminated; its lustre is shining and metallic; it is opaque; soft and brittle; its specific gravity from 4.3 to 4.9.

Copper Pyrites is a compound of sulphur, copper, and iron; or rather a combination of sulphuret of copper and sulphuret of iron, and these in various proportions. Its colour is brass-yellow, being deeper as the copper is more abundant in its composition; it is generally tarnished, and often iridescent. It occurs massive, disseminated, in botryoidal and stalactitic forms, and crystallized. Its lustre is shining and metallic; its fracture uneven; it is brittle, and has a specific gravity from 4.1 to 4.3.

The last of these sulphurets is the Grey Copper Ore. It contains, combined with sulphur and copper, various metals, lead, antimony, silver, and iron, in very variable proportions; and what proves it to be a proper sulphuret of copper, and that these are merely mixed with it, is that, when present, they do not materially modify its properties, and that it occurs composed of copper, iron, and sulphur alone; one specimen analysed by Chenevix having given 52 of copper, 31 of iron, and 14 of sulphur. It occurs massive, disseminated, and crystallized; the principal form of its crystals being the tetraedron or three-sided pyramid, variously modified. Its colour is steel-grey, which is liable to tarnish; its lustre is shining and metallic; its fracture uneven; it is brittle, and has a specific gravity from 4.4 to 4.8.

White Copper Ore appears to contain arsenic, from the odour it exhales when heated by the blowpipe, in combination with copper, and probably iron and sulphur. Its colour is white, with a shade of grey or yellow; its lustre is metallic; it is brittle, and has an uneven fracture; it occurs massive and disseminated, and is a rare ore.

SECT. VI.

ORES OF IRON.

Iron is of all metals the one of most extensive distribution. It occurs generally in the state of oxide, pure or combined with other substances, forming an extensive series of ores.

Besides these, the singular fact has been established, that it is a meteoric or atmospheric production, the stony masses which it has been established by the most ample evidence have fallen from the clouds at different periods, and in different countries, being composed principally of iron. As natural compounds of this metal, they may be considered in this place.

These meteoric stones are heterogeneous in their structure. They have externally a thin black crust. When broken they are of an ash-grey colour, and granulated texture, and appear to be composed of four substances, which can be distinguished by a lens. One is in small globular or elliptical grains of a grey colour, having a conchoidal fracture, a lustre resembling that of enamel, and so hard as to scratch glass; this has a resemblance in characters and composition to Chrysolite. Another consists of iron pyrites of a reddish yellow colour, and granulated texture. The third consists of particles of iron in a metallic state, capable of being extended under the hammer, and giving to the entire stone the property of being attracted by the magnet. These three substances are united by a fourth, which is nearly of an earthy consistence. Mr Howard first investigated the composition of these *. Both the metallic pyrites and the iron contain nickel. The vitrified substance consists of silica, magnesia, oxide of iron, and a little nickel. The composition of the earthy matter is nearly the same, and it differs principally in aggregation. The external crust consists of iron and nickel partially oxidated. In all the specimens the same elements were found, and in proportions not very different; and this agreement in fossils, found in countries so remote, is a proof of their common origin. These results were confirmed by the analysis of other meteoric stones by Vauquelin and Klaproth †; they found also portions of alumina and lime in their composition. Laugier detected chrome ‡, and this has been established by subsequent analyses. These have farther proved, that the composition is not altogether uniform; there is sometimes no trace of chrome, or of magnesia; the alumina is not often met with, though in some specimens its proportion is so large as 9 in 100 parts; the lime too is not always found, while it sometimes amounts to 12 in 100.

There can be no doubt, but that the large insulated

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* Philosophical Transactions, 1802.

† Philosophical Magazine, vol. xv. xvi.

‡ Nicholson's Journal, vol. xv. p. 147.

masses of iron which have been found in America and Siberia have had the same origin. Proust, in analysing a fragment of that from America, found it to contain nickel; Mr Howard, on repeating the analysis, likewise ascertained this, 100 grains giving 7½ of nickel. That from Siberia he equally found to contain nickel. And both these masses have a vitrified matter, resembling chrysolite, intermixed in their substance, analogous to that present in the meteoric stones. Other aerolites, as these substances have been named, have been found by Klaproth to consist of 94 or 97 of iron, with 3 or 4 of nickel. Native iron, evidently not meteoric, contains no nickel.

From many of the accounts authenticated with regard to the fall of these masses, it appears that they have been highly heated, and probably in a state of fusion. The stone, when touched after its fall, has been felt hot, and the external crust has appeared newly vitrified. The fall has been frequently accompanied with the appearance of a fiery meteor, as of a luminous ball, and sometimes with discharges of lightning, and with a loud noise, or explosions.

With regard to the origin of these masses, it is difficult to advance any hypothesis at all satisfactory. They have been supposed to be projected from volcanoes, a supposition refuted by the consideration of their entire dissimilarity to any known volcanic production, and of their fall in countries so remote from any volcanoes. La Place advanced the conjecture, that they have been projected from the moon, and endeavoured to shew by calculation, that a force might be exerted at the surface of that planet adequate to this effect,—a calculation involving, however, the assumption, that the moon has no atmosphere, and liable to other objections, derived from circumstances connected with their fall. The more probable hypothesis is obvious, that they may be the products of combinations in the upper regions of the atmosphere. And in favour of this it may be remarked, that some relations have been traced between the fall of these masses, and the state of the atmosphere as connected with the weather, the season of the year, the time of the day, and the latitude of the places where they have fallen *. There is also the appearance of a cloud from the part of the atmosphere whence the descent happens; a noise too accompanies or precedes it, and frequently a luminous discharge. These facts are favourable to the opinion, that they are formed by chemical changes occurring in the atmosphere; but in the present state of our knowledge of the elements of bodies, no possible combinations can be conceived giving origin to such products; and no conjecture even can be formed having the slightest appearance of precision.

Besides these, native iron with little alloy is sometimes, though rarely, found in the mineral kingdom. Klaproth found a specimen to be composed of 92.5 of iron, 6 of lead, and 1.5 of copper: and others similar have been discovered.

The most abundant and most numerous ores of iron are those in which it is mineralized by oxygen, of which there is a series differing in the degree of oxidation of the metal, and in the intermixture of other substances. These may be arranged, principally from their chemical relations.

One species well defined is that named Magnetic Iron Ore, from its high magnetic power. It occurs massive and crystallized; the forms of its crystals being the cube, octaedron, and rectangular tetraedral prism. Its colour is black, or deep grey; its lustre is shining and metallic; and it is opaque: its fracture is uneven, or imperfectly foliated; it is brittle and hard; its specific gravity is from 4.2 to 4.9; it is insoluble in nitric acid, but dissolves in muriatic acid, with the assistance of heat. It yields from 80 to 90 in 100 of iron, and may be regarded as a pure oxide. Sometimes it occurs in the form of small particles or grains, forming what is named Magnetic Iron Sand.

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* Annales de Chimie, tom. lxxxv. p. 262. Nicholson's Journal, vol. xxxv. xxxvi.

The next species is equally determinate,—that named Specular Iron Ore, or Iron Glance. In it the magnetic power is so far impaired by a higher degree of oxidation, that it is attracted by the magnet only when in fine powder. It occurs massive, and frequently crystallized; the forms of its crystals being very numerous, and variously modified; its colour is steel grey, often tarnished and iridescent; the lustre shining and metallic; the fracture uneven, sometimes foliated; it is so hard as to scratch glass, and is brittle; its specific gravity is from 4.6 to 5.2. It is insoluble in nitric acid, but dissolves in muriatic acid, with the assistance of heat. It consists of from 60 to 80 of iron, and from 20 to 30 of oxygen. Micaceous Iron Ore has been regarded as a variety of this species. It is massive, disseminated, or crystallized, in small and thin six-sided plates; is shining, and feels somewhat greasy, but without staining the fingers; and is not so hard as specular iron ore.

The next family of ores it is more difficult to arrange. The iron is in a higher state of oxidation, and the oxide is mixed with quantities of other substances, principally alumina, silica, and lime, but in such variable proportions, and passing so much into each other, that their specific distinctions can be only imperfectly determined. The principal of these ores are Red Ironstone, Brown Ironstone, Black Ironstone, and Clay Ironstone.

Of Red Ironstone, there are two principal varieties, the compact, the fracture of which is even; and the hæmatite, the fracture of which is fibrous, the fibres being straight, parallel, or diverging. The former occurs massive, or in nodules, or stalactitic, the latter almost always in globular or kidney-shaped masses, stalactitic or botryoidal. The colour of both is intermediate between brownish red and steel grey; but in the streak, and in powder, always blood red. Their specific gravity is from 3.5 to 5.

Brown Ironstone is distinguished from the red, principally by the colour being brown in the mass, and in the streak yellow, or yellowish brown. Of it, too, there are two principal varieties, distinguished by the fracture,—the compact brown ironstone, the fracture of which is even; and the brown hæmatite, the fracture of which is fibrous, the fibres being in general diverging. The compact occurs massive, sometimes of various imitative forms. The fibrous occurs in nodules, stalactitic, kidney-shaped, or botryoidal. The colour of both is brown, of various shades and intensities; sometimes tarnished, so as to be iridescent, with a degree of lustre that is semi-metallic: the specific gravity is about 3.4 or 3.5. The analysis has not been executed with accuracy, but both varieties appear to contain, with oxide or carbonate of iron, silica, lime, and oxide of manganese, in minute quantity. The iron, too, appears to be generally in the state of hydrated oxide; and the quantity of combined water amounts to about 15 in 100 parts. They yield from 40 to 60 of iron, in general of excellent quality, from 100 of ore.

Black Ironstone, like the red and brown, comprises two principal varieties,—the compact, and the fibrous or black hæmatite. Its colour is bluish black, or dark steel grey, with a semi-metallic lustre. It occurs massive, and in tuberose, kidney-shaped, and botryoidal pieces.

Argillaceous Iron Ore, or Clay Ironstone, comprises a series of ores, in which oxide of iron is combined more or less perfectly with carbonic acid, and mixed with earthy matter, chiefly alumina and silica, and which pass by variations of proportions into each other. The common clay ironstone occurs massive, generally in beds or strata. Its colour is grey, of different tints, passing into shades of yellowish or reddish brown, especially from exposure to the air; it has no lustre, and is perfectly opaque; its fracture is earthy; sometimes even; sometimes inclining to slaty; it is soft, feels meagre, adheres a little to the tongue; its specific gravity is about 3.3 or 3.4. Consists of from 30 to 50 of oxide of iron, from 10 to 20 of silica, 15 to 40 of alumina, about 28 or 30 of carbonic acid, with small portions of manganese. The ores of this family have been generally supposed to consist of oxide of iron and clay, with portions of lime and silica; according to Descostils*, their basis is carbonate of iron, the same as the sparry iron ore, with silica, and small portions of alumina, lime, magnesia, and manganese. They afford from 30 to 40 of iron in 100, of good quality. Nodular Ironstone, reniform iron ore, or eagle stone, belongs to this species; it occurs in rounded masses, sometimes spherical, generally oblate, composed of concentric lamellar concretions, and sometimes inclosing a nodule slightly adhering or quite loose. Pisiform Iron Ore is a similar variety, in small rounded grains, whence its name; of a yellowish brown colour, having an earthy fracture, with little coherence.

Sparry Iron Ore is a species well determined from its chemical relations. It consists of carbonates of iron and manganese, and carbonate of lime, though in very variable proportions. The proportion of carbonate of lime augments in some varieties so much, that they are referred to the calcareous fossils, forming the Pearl Spar; and it is only when the proportion of metallic matter is abundant, that it is regarded as an iron ore. It occurs massive, disseminated, and crystallized; the forms of its crystals being the rhomb, perfected or truncated, the lens, the octaedron, and the dodecaedron. Its colour is white, grey, yellow, or brown; but what is a peculiar character, the colour darkens on exposure to the air, from absorption of oxygen; it thus becomes brown, and at length black; its lustre is pearly; it is translucent on the edges; its fracture is foliated; its fragments are rhomboidal; its specific gravity is from 3.6 to 3.8; it is soluble with effervescence in acids. It blackens before the blowpipe, and loses weight. The results of analysis with regard to its composition are so discordant, that it is scarcely possible to assign the precise composition. Bergman obtained from different specimens

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* Annales de Chimie, tom. lxxxiv. p. 188.

from 22 to 38 of oxide of iron, from 24 to 28 of oxide of manganese, from 19 to 24 of lime, from 10 to 17 of carbonic acid, and from 9 to 6 of water. Descostils found, that along with much variation in the proportion of manganese, there were varieties in which the lime was in inconsiderable quantity, or entirely wanting, while in others magnesia was present, but not in any uniform proportion. And Drappier obtained a similar result, and found also in some where magnesia was present, neither manganese nor lime. There can be little doubt, that in such cases different species are confounded from similarity of external characters; and that the diversity arises from the numerous and apparently indefinite proportions in which carbonate of lime, and of magnesia, of iron, and of manganese, enter into combination.

Pitch Iron Ore occurs in layers of a greyish black colour, with resinous lustre. It consists of oxide of iron and water, with a little sulphuric acid.

Oxide of iron deposited from stagnant water, in swampy situations, forms Bog or Swamp Iron Ore, which is in masses corroded, or cellular, of a yellow or brown colour, dull, and earthy. With oxide of iron, the different varieties contain oxide of manganese, alumina, silica, and phosphoric acid: Vauquelin discovered in them also lime, magnesia, manganese, and chrome.

Blue iron earth has been supposed to be of similar origin, as it is sometimes associated with bog iron ore of an earthy form; and consists of oxide of iron and phosphoric acid and water, with variable proportions of alumina and silica: its colour is indigo blue: it is massive, friable, and without lustre. Iron mineralized by phosphoric acid, constitutes a proper species, which occurs in slender crystals, or in small plates adhering slightly, the surface of which is brilliant, and of a blue colour; they are translucent, but some, apparently from the loss of water, are opaque. The specific gravity is 2.6. The composition is 41 of oxide of iron, 19 phosphoric acid, 1.3 of silica, 5 of alumina, and 32 of water.

Iron mineralized by arsénic acid, forms an ore, formerly regarded as an arseniate of copper. It occurs massive or crystallized in small cubes, translucent, smooth, and highly shining, the lustre being adamantine; the colour is dark green, sometimes with a brown or yellowish tinge. The fracture is imperfect foliated: the specific gravity 3000. Analysed by Chenevix, this species was found to consist of 31 arsénic acid, 45.5 oxide of iron, 9 oxide of copper, 4 of silica, and 16.5 of water. The copper he regards as accidental, not essential to the composition. There is another, however, in which it is more constant, and in larger proportion, the proportions being 33.5 arsénic acid, 27.5 oxide of iron, 22.5 oxide of copper, 3 of silica, and 12 of water. This occurs in minute crystals, of a faint sky blue colour; transparent, and of very high lustre, and generally grouped irregularly, sometimes united so as to assume a mammillary form.

Iron, in combination with sulphur, forms a well defined species, known under the name of Pyrites. It occurs massive, disseminated, and often crystallized; the usual form of its crystals is the cube regular or modified by truncation of the angles or edges, or acumination of three planes on the angles. Its colour is brass yellow, and the lustre metallic: it is opaque. The fracture is uneven. It is brittle; its hardness is such as to strike fire with steel; its specific gravity is from 4.6 to 4.8. By friction it exhales a sulphureous smell. This odour is strong when it is heated before the blowpipe: it gives also a blue flame. Various analyses of it have been given; the proportions in the common pyrites, according to the analysis by Hatchet, are 52 of sulphur, with 48 of iron.

There are some varieties of this species. The Striated or Radiated Pyrites presents a striated fracture, the striæ being diverging. Capillary Pyrites occurs in capillary crystals, having a metallic lustre, and a colour passing from yellow to steel grey. Hepatic Pyrites, so named from the liver brown colour it assumes from exposure to the air, occurs massive and crystallized in six-sided prisms, or six-sided pyramids: has less lustre than the others, and is more subject to decomposition.

Magnetic Pyrites, distinguished by its magnetic quality, forms a distinct species. Its yellow colour is deeper, and approaching to brown, often tarnished; its lustre is inferior, but metallic. Its fracture is compact; it is hard and brittle; its specific gravity is 4.5. It occurs massive or disseminated. It is a sub-sulphuret, the proportions, according to Mr Hatchet's analysis, being 36.5 of sulphur, and 63.5 of iron.

SECT. VII.

ORES OF LEAD.

Lead occurs principally mineralized by different acids, and by sulphur.

Carbonate of Lead, the White Lead Ore of mineralogists, is presented under different forms,—earthy, indurated, and crystallized. The figures of its crystals are the hexaedral prism, the tetraedral prism, the double hexaedral pyramid, the four and the six-sided table; it occurs also in acicular crystals, aggregated and intersecting. The surface of the crystals is highly shining, the lustre adamantine; the colour white, sometimes grey, yellowish, or brown; they are transparent, or translucent; are brittle and soft. The specific gravity is from 6 to 7. When massive, it has less lustre and transparency. Urged by the flame of the blowpipe, it decrepitates, becomes yellow or red, and melts into a metallic globule. It effervesces with acids, and in diluted nitric acid is dissolved. Its composition varies with regard to the proportions of its constituent parts; and it often contains variable quantities of oxide of iron, alumina, silica, and lime. A specimen of it pure, was found by Klaproth to be composed of 77 of lead, 5 of oxygen, 16 of carbonic acid, and 2 of water.

Earthy Lead Ore, which occurs friable or indurated, without lustre or transparency, appears to be a mixture of carbonate of lead with earthy matter. When associated with an ochrey earth, so as to assume a red colour, it has been named Native Minium. Black Lead Ore appears to be carbonate of lead, altered by the action of sulphur, or by intermixture with it; it is found generally incrusting the native sulphuret, and is itself incrusted by the carbonate. A lead ore, crystallized in cubes, similar in appearance to carbonate of lead, but softer, and having less specific gravity, was found by Chenevix to contain both carbonic and muriatic acid.

Lead occurs mineralized by sulphuric acid, usually crystallized; the form of the crystals being the octaedron, modified by truncation or bevelment. Its colour is white; the crystals are transparent, or semi-transparent; their lustre shining and adamantine; the fracture compact; the specific gravity 6.300. It does not effervesce with acids, and is not soluble in nitric acid. It consists of oxide of lead 71, sulphuric acid 24.8, water 2, oxide of iron 1.

Phosphate of lead is a common ore. Its usual colour is green; but it passes through yellowish green into pure yellow. It occurs in an incrustation, often mammillary or botryoidal, composed of minute crystals aggregated, or in larger crystals in hexaedral prisms, and hexaedral pyramids. They have a waxy lustre, and are translucent; the fracture is uneven; it is brittle and soft. The specific gravity is from 6.2 to 6.9. It does not decrepitate before the blowpipe, but becomes white, and melts into a globule of a grey colour, without the lead being reduced. It does not effervesce with nitric acid, but is dissolved by it. It was found by Klaproth to consist of oxide of lead from 78 to 80 parts, phosphoric acid 18 or 19, muriatic acid 1.5 or 1.7, and a minute trace of oxide of iron. Brown Lead Ore, which occurs massive, and crystallized in hexaedral prisms, having a waxy lustre, and opaque, Klaproth found to consist of oxide of lead 78.58, phosphoric acid 19.73, muriatic acid 1.65.

Lead occurs mineralized by phosphoric and arsenic acids, forming an ore in mammillary masses, of a yellowish green colour. The pure arseniate also occurs. Its colour is green, which passes to yellow; it occurs in acicular or capillary crystals, and also massive. Another variety of arseniate of lead, with an intermixture of iron, occurs in masses of a rough surface of a yellow colour, opaque and dull. These are all distinguished by the strong arsenical odour they give when heated on charcoal by the blowpipe.

Yellow Lead Ore is a species, in which the lead is mineralized by molybdic acid. It occurs massive, or in small crystals, rectangular tables of four or eight sides, cubes, or octaedrons. Its colour is wax-yellow, and its lustre waxy; it is translucent, is soft, and easily broken. It decrepitates before the blowpipe, and melts into a globule of a grey colour, in which are disseminated particles of metallic lead; is insoluble in nitric acid. It consists of oxide of lead 58.40, molybdic acid 38, oxide of iron 2.08, and silica 0.28.

Lead, mineralized by sulphur, forms the most abundant ore of the metal, that named Galena. It occurs massive, disseminated, incrusting, in corroded or reticulated masses, and crystallized. The forms of its crystals are the cube, the octaedron, the tetraedral prism, the hexaedral prism, and the three-sided table, perfect or modified by truncation, acumination, or bevelment. Its colour is bluish or lead grey, sometimes inclining to black, and sometimes iridescent. Its lustre is splendent and completely metallic; it is perfectly opaque; its fracture is distinctly foliated; its fragments are of a cubical form: it is soft, so as to be easily scratched; it is also easily frangible; its specific gravity is from 7 to 7.7. It decrepitates before the flame of the blowpipe, melts, exhales a sulphureous odour, and affords a globule of lead. The proportions of lead and sulphur vary considerably; that of the lead is from 50 to 83, of the sulphur from 10 to 25. The proper proportion, exclusive of extraneous ingredients, is that of 84 with 16; and there is a sub-sulphuret containing only 25 *per cent.* of sulphur. There are also always present small portions of silver, iron, silica, and lime. One variety which is of an uneven fracture, compact galena, contains a little sulphuret of antimony. In another the sulphuret of antimony is so large, that it forms a distinct species, named Bournonite; it is of a grey colour, occurs massive, and sometimes crystallized in the form of a cube; its specific gravity 5.7: consists of sulphurets of lead and antimony, with smaller portions of sulphuret of copper and iron.

SECT. VIII.

ORES OF TIN.

TIN occurs in nature principally in the state of oxide, and in smaller quantity in that of sulphuret.

Native oxide of tin, or Tinstone, occurs massive, disseminated, and crystallized. The forms of its crystals are very complicated and imperfectly marked. Its colour is brown, of various shades. Its lustre is shining, and, externally in the crystals, highly splendent; it is opaque; or when of a light shade, translucent, or semi-transparent; its fracture is uneven; it is hard and brittle; its specific gravity is from 6.3 to 6.9. It decrepitates before the blowpipe, and, when heated on charcoal, is reduced. It is nearly a pure oxide. A specimen analysed by Klaproth gave 77.5 of tin, 0.25 of iron, 21.5 of oxygen, and 0.75 of silica.

Wood Tin Ore consists of oxide of tin, with from 0.05 to 0.10 of oxide of iron. It is found in small rolled pieces or fragments, and has a distinctly fibrous fracture. Its colour is brown; its lustre glistening; it is opaque, hard, brittle, and has a specific gravity of 6.456.

Tin mineralized by sulphur, with copper and a little iron, ſorms Tin Pyrites. It occurs massive or disseminated; its colour is steel-grey, passing into yellowish grey; its lustre is metallic and shining, or glistening; it is opaque; its fracture is uneven; it is semi-hard, brittle, and has a specific gravity of 4.350. It is composed of 25 of sulphur, 34 of tin, 36 of copper, and 2 of iron.

SECT. IX.

ORES OF ZINC.

Zinc is mineralized by oxygen, carbonic acid, sulphuric acid, and sulphur.

Its most abundant ore, Calamine, occurs earthy, or without much induration, sometimes more highly indurated, of a compact or striated texture. It is massive, cellular or corroded, or botryoidal, sometimes in minute crystals, forming a drusy incrustation. Its colour is white, with various shades of yellow; it is dull, translucent; the crystals are nearly semi-transparent; the earthy is opaque. Its specific gravity is from 3.5 to 4. It becomes electric by heat; when heated before the blowpipe, it becomes white, but is not reduced. Some varieties effervesce with acids; others do not; they dissolve in nitric acid, forming a solution of a gelatinous consistence. The composition varies much. Some appear to be composed only of oxide of zinc and silica, with or without water. Thus Klaproth found a specimen to consist of 66 of oxide of zinc, and 33 of silica; and Pelletier another, of oxide of zinc 36, silica

52, and water 12. More generally carbonic acid is present, and then the silica is wanting. Mr Smithson analysed several of these varieties, and found the proportions to be about 65 of oxide of zinc, and 35 of carbonic acid; in some water was present. Calamine probably forms two species, the one carbonate of zinc, the other oxide of zinc with silica. It is the latter which forms a gelatinous solution with acids, and becomes electric by heat.

A red ore of zinc has been found in the United States of America, which consists of the oxide, with small portions of oxides of manganese and iron: it is massive, hard, brittle, and has a foliated fracture.

Blende, or native sulphuret of zinc, presents several diversities in appearance. From difference of colour, three sub-species have been formed, the yellow, the brown, and the black: of which the brown is the most common. Its colour is brown, with shades of yellow and red, and often tarnished; its lustre is splendent, inclining to resinous; it is more or less translucent; its fracture is foliated, sometimes fibrous; it is semi-hard, brittle, and has a specific gravity of from 3.7 to 4. It occurs massive and disseminated, and often crystallized; the forms of its crystals being both numerous and complicated. Yellow blende has a yellow colour of various shades, passing into green or red; its lustre is rather greater, and is adamantine; and when the colour is light, it is semi-transparent. Black blende has a black colour, with a shade of brown or red; its lustre is metallic; its fracture foliated; it is opaque or translucent on the edges. Blende, in addition to zinc and sulphur, contains usually a portion of water, about 4 or 6 *per cent.*; and frequently small portions of iron, lead, silica, and alumina. The proportion of zinc in the different varieties is from 45 to 65, and of sulphur from 17 to 30. According to Bergman, the yellow contains fluoric acid.

SECT. X.

ORES OF BISMUTH.

Bismuth occurs native, mineralized by oxygen, and by sulphur.

Native bismuth has the properties of the pure metal. Its colour is white verging to red, and often tarnished, with metallic lustre; its fracture is foliated. It occurs massive, disseminated, sometimes crystallized, in four-sided tables, or cubes, small and indistinct. It melts even in the flame of a candle.

Oxide of bismuth occurs in an incrustation of a yellowish grey colour, earthy, or when indurated, having an uneven or foliated fracture; dull when earthy, shining when foliated, opaque and soft.

Sulphuretted bismuth occurs massive, disseminated, and in capillary crystals, of a light grey colour, and shining metallic lustre. It melts in the flame of a candle, and when heated, exhales sulphurous fumes. It consists of 60 of bismuth and 40 of sulphur. A variety, or perhaps a different species, occurs also massive and crystallized in acicular prisms, of a steel-grey colour, in which it is associated with portions of lead and copper.

SECT. XI.

ORES OF ANTIMONY.

This metal is found native, combined with oxygen and muriatic acid, and mineralized by sulphur.

Native antimony is of very rare occurrence. It has the usual characters of the metal, and contains a very minute portion of silver and iron.

Antimonial Ochre occurs as an earthy-like incrustation, of a straw-yellow colour, and has been supposed to be an oxide. Another ore, which had been supposed to be a muriate, but appears to be an oxide, is the White Antimonial Ore, occurring in acicular crystals, aggregated, so as to form a stellular appearance, and in tables and in cubes, of a snow-white colour, silky lustre, translucent and soft. Its composition, as stated by Vauquelin, is 86 of oxide of antimony, 3 oxides of antimony and iron, and 8 of silica.

The sulphuret is the principal antimonial ore. It occurs massive, disseminated, or crystallized, its crystals being acicular or prismatic, and often aggregated. Its colour is lead-grey, frequently tarnished or iridescent; its lustre is shining and metallic: it is opaque. Its fracture is striated or radiated; in one variety foliated, in another small grained uneven. It melts easily before the blowpipe, and exhales fumes of sulphur and oxide of antimony. It consists of 74 of antimony, and 26 of sulphur. Plumose Grey Antimonial Ore contains, with sulphuret of antimony, portions of arsenic and iron, and sometimes a little silver. It occurs generally in capillary crystals.

Red Antimonial Ore is probably a sulphuretted oxide, its composition, as found by Klaproth, being 67.5 of antimony, 10.8 of oxygen, and 19.7 of sulphur. It occurs in capillary crystals of a red colour, opaque, and shining. It melts before the blowpipe, and exhales in vapour.

SECT. XII.

ORES OF ARSENIC.

Arsenic is found native, pure, or alloyed with other metals; and also mineralized by sulphur, by oxygen, and in the state of acid with lime.

Native arsenic is of a white colour, with a slight shade of grey, with metallic lustre; but tarnishes quickly on exposure to the air, changing its colour, and losing its lustre. It occurs massive and disseminated; its fracture is uneven; it is semi-hard, very brittle, and has a specific gravity of 5.6 or 5.7. It generally contains a portion of iron, with sometimes a little silver or gold.

With a larger quantity of iron, and a small quantity of sulphur, the species named Arsenical Pyrites, or Mispickel, is formed. Its colour is white, but it quickly tarnishes, and becomes yellow; the lustre of its fresh fracture is shining and metallic. It occurs massive, and often crystallized; the form of its crystals being the tetraedral prism, and octaedron very acute. Its fracture is uneven; it is hard and brittle; has a specific gravity of from 5.7 to 6.5. Consists of arsenic 43, iron 35, sulphur 21.

Argentiferous Arsenical Pyrites differs little from the preceding species: its colour is silver-white, with a yellow tarnish, its lustre metallic: with arsenic and iron it contains a portion of silver, varying from 1 to 10 in 100 parts.

Arsenic, mineralized by sulphur, forms two ores, named Orpiment and Realgar. Realgar is of a red colour, scarlet, or orange. It occurs massive, and crystallized in oblique tetraedral or hexaedral prisms; translucent, or semi-transparent, with a shining lustre. It exhales before the blowpipe a white arsenical smoke, and gives a blue flame. Orpiment is of a yellow colour, with a highly shining lustre, is translucent, or semi-transparent when in thin leaves. It occurs massive, and in very minute crystals. Its fracture is foliated; it is soft and somewhat flexible: it exhibits the same appearances before the blowpipe as the other. It differs from the red, in containing a larger proportion of sulphur. The orpiment, according to Klaproth, consists of 62 of arsenic, and 38 of sulphur; the realgar of 69 of arsenic, and 31 of sulphur. Both, according to Laugier, contain more arsenic than the artificial sulphuret, and this excess he considers in both as merely adventitious.

Native oxide of arsenic occurs as an incrustration on other ores, friable or little indurated, sometimes botryoidal, or in minute crystals.

Arsenic, in the state of acid united with lime, forms the ore named Pharmacolite. This occurs as an incrustation, botryoidal, or in capillary crystals, of a white colour: translucent on the edges, with a silky lustre; its fracture is striated; it is soft, and light, the specific gravity being 2.5 or 2.6. It dissolves in nitric acid, and gives the arsenical odour by the blowpipe. It contains 25 of lime, 50.5 arsénic acid, 24.5 water.

SECT. XIII.

ORES OF COBALT.

The ores of cobalt are distinguished by giving to borax, when fused with it, a blue colour, and forming a solution with nitro-muriatic acid, which becomes green from heat.

White Cobalt Ore is an alloy of cobalt and arsenic, with a little sulphur and iron, the two latter being probably accidental. Its colour is tin-white, liable to tarnish, and thus assume a grey or reddish tinge; its lustre is weakly shining and metallic. It occurs massive and crystallized in cubes, and in octaedrons; the fracture is uneven; it is hard and brittle. Before the blowpipe it melts, and gives an arsenical smoke and odour; it forms a metallic globule, and gives to borax a blue colour. To this species probably belongs the Shining Cobalt Ore, or Cobalt Glance: the colour, lustre, fracture, forms of crystallization, and the chemical characters, being the same.

Grey Cobalt Ore appears to be an alloy of cobalt with arsenic and iron, containing also silica or silicon; sometimes with small portions of nickel and bismuth. Its colour is light grey, liable to tarnish; its lustre weakly shining and metallic: its fracture is even; it is semi-hard, passing into hard; brittle; its specific gravity is from 5.5 to 7.7. Before the flame of the blowpipe, it gives an arsenical odour and smoke; to borax it gives a blue colour.

Oxide of Cobalt occurs in a loose form, or of various degrees of induration, but always dull, and earthy in its fracture, soft, and easily broken. It is of different colours, from the intermixture of oxide of iron, and other metallic oxides; whence varieties, distinguished by the names of Black, Brown, and Yellow Cobalt Ochres. These all give a blue colour to glass or to borax when fused with it, and sometimes exhale an arsenical odour.

Red or Peach Bloom Cobalt Ore derives its name from its colour, which is a beautiful red, similar to that of the peach blossom, passing, however, into other shades of red. It occurs massive, disseminated, and in minute crystals. One variety has an earthy fracture, without lustre, and occurs as an incrustation. Before the blowpipe it loses colour, becomes grey, and gives a weak arsenical odour; borax receives a rich blue colour. This species appears to be arseniate of cobalt. According to Bucholz, it consists of cobalt 39, arsénic acid 38, water 23.

SECT. XIV.

ORES OF NICKEL.

Nickel occurs alloyed with arsenic, and a little sulphur; and also in the state of oxide. The first species, the Kupfer-nickel of mineralogists, is the most abundant. It occurs massive and disseminated; its colour is copper-red, of various shades; its lustre is weakly shining and metallic: it is opaque; its fracture is uneven; it is hard, and not easily broken; its specific gravity is from 6.6 to 7.5. Before the flame of the blowpipe, it gives arsenical vapours. It dissolves in acids, giving a green solution. Bergman found it to be composed of nickel, iron, cobalt, arsenic, and sulphur. Vauquelin regards it as an alloy of nickel and arsenic, the others being accidental.

Oxide of nickel occurs as an incrustation, sometimes disseminated, of a friable texture and earthy appearance; of an apple-green colour, without lustre. Its solution in acids is of a green colour. It occurs generally with kupfer-nickel, or with certain cobalt ores.

SECT. XV.

ORES OF MANGANESE.

THE principal ore of manganese is the Black Oxide. It occurs massive, or in crystals of the form of rhomboidal tetraedral prisms. Its usual colour is steel-grey, inclining to brown or black, and varying in lustre: when crystallized, the surface of the crystals is shining: when amorphous, it is more dull. Its texture is radiated, foliated, compact, or earthy. The specific gravity varies from 3.5 to 4.7. All the varieties have the same chemical characters. They are not melted by the blowpipe, but assume a brown colour. To borax they communicate by fusion a violet-blue colour. The radiated variety appears to be a pure oxide, composed, according to Vauquelin's analysis, in one specimen, of 92.75 of oxide of manganese, and 7 of water; in another, of 99.25 of oxide, with 0.25 of water. But there are also frequently present oxide of iron, carbonate of lime, silica, and barytes. The earthy variety contains the largest proportion of oxide of iron. And what has been named Black Wad, which occurs as an earthy incrustation, consists of 43 of oxide of manganese, and 43 of oxide of iron.

Red Manganese Ore consists of the oxide with silica and lime. Its colour is rose-red, more or less pale, passing, from exposure to the air and light, to light yellow, or even to white. It has little lustre or transparency; occurs massive and disseminated; its specific gravity is 3.233. Before the flame of the blowpipe it does not melt, but acquires a dark grey colour: to borax it gives, by fusion, a violet tinge. According to a late analysis by Berzelius, it is composed of oxide of manganese 54.42, silica 48, lime 3.12.

Oxide of manganese, combined with 0.15 of sulphur, forms an ore of a black colour, shining lustre, opaque, soft, and massive.

Phosphate of manganese and iron occurs massive, of a brownish black colour, resinous lustre, and semi-transparent in thin pieces.

SECT. XVI.

ORES OF MOLYBDENUM.

There is only one proper ore of this metal—the sulphuret, or what is called molybdena. It occurs massive, disseminated, and sometimes crystallized in hexaedral prisms or tables. Its colour is lead-grey, its lustre metallic, its fracture is foliated, and it is easily split; it is soft, so as to soil; and feels unctuous. Its specific gravity is from 4 to 4.7. It emits a white smoke before the flame of the blowpipe. It consists, according to Klaproth and Bucholz, of 60 of molybdena, and 40 of sulphur.

Oxide of molybdenum is said to occur sometimes as an incrustation on the sulphuret, of a yellow colour. And the molybdic acid or oxide, in combination with lead, forms one of the ores of that metal.

SECT. XVII.

ORES OF TUNGSTEN.

The mineral named Tungsten consists of the oxide or acid of the metal with lime, the proportions, according to Berzelius, being 80.5 with 19.5. It occurs massive disseminated, and in octaedral crystals. Its colour is yellowish or greyish white; its lustre shining and vitreous; it is translucent or semi-transparent, is soft, has a foliated fracture, and a specific gravity from 5 to 6.

The other species of this genus is the mineral named Wolfram. It occurs massive and crystallized in broad hexaedral prisms, or four-sided tables. Its colour is black, its lustre shining; it is opaque; its fracture is foliated; its specific gravity is 7.1. It consists of 78 oxide of tungsten, 18 oxide of iron, and 6 oxide of manganese.

SECT. XVIII.

ORES OF CHROME.

Chrome is found in the state of acid with oxide of lead, and in that of oxide or acid with oxide of iron.

Chromate of Lead, the red lead ore of mineralogists, is usually crystallized in rhomboidal four-sided prisms. Its colour is aurora red, it's lustre shining and adamantine: it is translucent; its specific gravity is 6. It consists of 64 of oxide of lead, and 36 of chromic acid.

Chromate of Iron occurs massive, and crystallized in octohedrons, is of a dark brown or black colour, sometimes with a shade of purple, dull, and opaque; hard, difficult to break, with an uneven fracture; its specific gravity is 4. Heated with borax by the blowpipe, it forms a vitreous globule of a fine green colour. It consists of oxide of chrome 55.5, oxide of iron 33, alumina 6, silica 2, and 3.5 of loss.

SECT. XIX.

ORES OF TELLURIUM.

THIS metal occurs chiefly alloyed with other metals.

In native tellurium the proportion is 90 in 100 parts, with portions of iron and gold. It is massive, or in small crystals of a white colour, and shining metallic lustre, having a foliated fracture, and a specific gravity from 5.7 to 6.1.

In graphic gold ore there is more gold, with a portion of silver, the proportions being 60 of tellurium, 30 of gold, and 10 of silver. It is usually crystallized in minute prisms, superficially aggregated on quartz. Its colour is steel-grey, its lustre metallic, but liable to tarnish, its fracture uneven, its specific gravity 5.7.

In the white or yellow sylvanite, there is present a portion of lead, with tellurium, gold, and silver. Its colour is silver-white, inclining to yellow; its lustre metallic; its fracture foliated; its specific gravity 10.6. It occurs disseminated, or in minute crystals.

In the black tellurium ore, the composition, as stated by Klaproth, is tellurium 82, lead 5.4, gold 9, copper 1.3, silver 0.5, and sulphur 3. It occurs massive, and crystallized in six-sided tables; its colour is blackish-grey; its lustre metallic; its fracture foliated; its specific gravity 8.9.

SECT. XX.

ORES OF TITANIUM.

Under this genus are placed several species, differing much in external characters.

Rutile, Titanite, or Red Shorl, is nearly a pure oxide of titanium. It occurs crystallized in prisms, often capillary, and penetrating quartz; its colour is red or reddish brown; its lustre shining; it is slightly translucent; it is hard and brittle; its specific gravity is 4.1. It becomes opaque and dull before the blowpipe, but does not melt; with borax it forms a yellow vitreous globule.

Sphene occurs in rhomboidal four-sided prisms and octohedrons, of a reddish brown colour, passing sometimes into yellow or green, with a shining lustre; translucent: it appears to be a combination of oxide of titanium, silica, and lime, in variable proportions.

Oisanite, octahedrite, or blue shorl, is regarded by Vauquelin as a pure oxide of titanium, differing from rutile in being free from iron, but probably existing in a different degree of oxidation. It is crystallized in acute octohedrons; its colour is blue, passing into brown; its lustre is shining and adamantine: it is translucent or semi-transparent; its specific gravity 3.8.

Menachanite occurs in grains or sand, of a greyish black colour, opaque, with semi-metallic lustre, having a specific gravity of 4.4, and weakly attracted by the magnet. It consists of oxide of iron 51, oxide of titanium 45.25, oxide of manganese 0.25, and silica 3.5. Nigrine is in angular grains of a brownish black colour, with little lustre, and opaque; its specific gravity is 4.5; it is not attracted by the magnet; it consists of 84 of oxide of titanium, 14 of oxide of iron, and 2 of oxide of manganese.

Iserine occurs likewise in angular grains, of a black colour and weak lustre, and opaque, having a specific gravity of 4.5. It consists of oxide of titanium 59.1, oxide of iron 30.1, and oxide of uranium 10.2.

SECT. XXI.

ORES OF URANIUM.

THE mineral named Pechblende is the ore in which this metal was first discovered. It is generally massive, of a black colour, with an internal lustre shining and resinous; opaque, brittle, and soft; having a specific gravity of 7.5. It consists of 86.5 of oxide of uranium, with 6 of sulphuret of lead, 5 of silica, and 2.5 oxide of iron.

Green Mica, or Micaceous Uranitic Ore, is oxide of uranium 74.5, with 15.5 of water mixed with 8.2 of oxide of copper. It occurs in thin leaves, or in minute four-sided tables; its colour is green; its lustre shining, with transparency; its fracture is foliated; and it is soft.

Uranitic ochre occurs as an incrustation or efflorescence, of a straw yellow colour, without lustre, opaque, soft, and friable. It is oxide of uranium nearly pure, containing sometimes a little oxide of iron.

SECT. XXII.

ORES OF TANTALUM.

THE mineral named Tantalite has been considered as an alloy of tantalum with iron and manganese; according to Berzelius, it is oxide of tantalum with small portions of oxides of manganese and iron: 83.2 of the first, 7.4 of the second, and 7.2 of the third. It occurs in imperfect octaedral crystals of a black colour, with an internal metallic lustre; hard so as to give sparks with steel, and having a specific gravity of 7.9.

Ittrotantalite was considered as composed of tantalum, or oxide of tantalum, with iron and a portion of ittria; but from a more recent analysis by Berzelius, is more complicated. The composition is from 50 to 60 of oxide of tantalum, from 20 to 39 of ittria, from 1 to 8 of acid of tungsten, with small portions of oxides of iron and of uranium, and of lime. It is in small masses, or in prisms, of a dark brown yellow, or grey colour; opaque, with metallic lustre; a granulated fracture, and a specific gravity of 5.1.

SECT. XXIII.

ORES OF CERIUM.

In a mineral named False Tungsten, the metal Cerium was first discovered. It has since been named Cerite. It occurs massive or disseminated; of a flesh red colour, semi-transparent; and having, in the fresh fracture, considerable lustre; it is so hard as to strike fire with steel; and has a specific gravity of from 4.7 to 4.9. It consists, according to Hisinger, of oxide of cerium 68.6, silica 18, lime 1.25, oxide of iron 2, water and carbonic acid 9.6.

Ittrocerite occurs massive, of a grey, violet, or red colour, opaque, with glistening lustre; fracture foliated; specific gravity 3.4. Before the blowpipe loses its colour, but does not melt. It consists, according to Berzelius, of from 16 to 18 of oxide of cerium, with 48 or 50 of lime, 9 of ittria, and 25 of fluoric acid; is probably, therefore, a compound of fluates, with these bases.

Dr Thomson found in another mineral, which he named Allanite, 34 of oxide of cerium, with 25.4 oxide of iron, 35.4 silica, 9.2 of lime, and 4.1 of alumina. It is crystallized in prisms, of a brownish black colour, lustre resinous; opaque, semi-hard, and brittle; specific gravity 3.6. It swells before the blowpipe, and melts imperfectly.

CHAP. IV.

INFLAMMABLE MINERALS.

Under this order are placed those minerals not metallic, which have the property of inflammability. They admit of being arranged under three genera, resting on chemical distinctions. Sulphur constitutes one genus. Under a second may be placed those composed of Carbon principally,—the Diamond, Plumbago, and Coal. To a third I have referred the Bitumens: these consist chiefly of carbon and hydrogen, forming a series in which these principles are combined in different proportions, the hydrogen being usually predominant. Under this genus may probably be placed Amber, and Mellite or Honey-stone.

SECT. I.

NATIVE SULPHUR.

Sulphur occurs in the mineral kingdom principally as a volcanic product, though it is also found not of volcanic origin, disseminated in gypsum or limestone. It is usually pure, of its characteristic yellow colour, semi-transparent, or sometimes transparent, with shining lustre; it occurs massive, disseminated, stalactitic, or crystallized, the form of its crystals being the pyramid, octohedron, or dodecaedron under various modifications. It also occurs in masses, and as a light sublimate. Its other physical and its chemical properties are those of pure sulphur.

SECT. II.

CARBONACEOUS MINERALS.

Of these the Diamond is the purest. From its external characters it has been placed among the earthy fossils; but as it is inflammable, and its nature perfectly ascertained, it must, in conformity to its chemical relations, be placed under the present genus, though differing widely from the other substances with which it is associated.

The Diamond is not met with in its original situation, but in the beds of streams, or in a loose ferruginous sand beneath the soil, either in perfect crystals, or in fragments often encrusted with a hard coating. The usual forms are the octohedron and dodecaedron variously modified, and generally imperfect. It is colourless, or tinged of various colours; is transparent, and has a high degree of refraction; its lustre is resplendent, and it is distinguished by the beautiful play of colours it exhibits; its fracture is lamellated, and it can be split by striking it in the direction of the plates. Its hardness is such that it is not impressed by steel. Its specific gravity is from 3500 to 3600.

Plumbago, or Graphite, is a carburet of iron, the proportion of the metal, in different specimens, being very various; and there being often an intermixture of silica and alumina; the pure carburet seems to consist of 91 of carbon, and 9 of iron. Graphite occurs massive, or disseminated; its colour is black, or dark steel grey; its lustre is weakly shining and metallic; it is opaque; its fracture is compact, foliated, or slaty; it is soft, soils the fingers, and feels unctuous; its specific gravity is from 2.1 to 2.6. It burns with difficulty, and consumes slowly, leaving oxide of iron as a residuum mixed with alumina and silica.

Coal consists of carbonaceous matter, and in one variety, the blind coal, this is nearly pure; but in the greater number of the varieties of coal, there is present a soft bituminous matter, which communicates some peculiar properties. Those which contain much bitumen are highly inflammable, take fire readily, and burn with a bright flame: those in which the proportion of bitumen is less, and in which the carbon predominates, burn less vividly; they require a higher heat to kindle them, and burn without flame, or only with a red glow. Numerous varieties of coal exist, deriving distinctions partly from their state of aggregation, but principally from the proportions of bitumen and carbon. The series may be described as they are connected, on the one hand, with vegetable matter, and on the other, with carbon not of vegetable origin.

Blind Coal, the Anthracite of mineralogists, the Glance Coal of Werner, consists almost entirely of carbon, with a little earthy matter and iron, and forms the connection of coal with plumbago. It burns with difficulty, without flame, without exhaling any bituminous odour, and without softening or caking; its colour is black; its lustre shining, and nearly metallic; its fracture is conchoidal or slaty; it is brittle, and has a specific gravity of about 1.5. It occurs often in primitive rocks, or in those of transition, in imbedded masses, in beds and veins; and there is no reason to infer that it is of vegetable origin.

Black Coal, as it is named by Werner, is the common coal, of which there are several varieties. That which is of a slaty fracture is the variety most abundant in this country; its principal fracture is slaty, the cross fracture small grained uneven; its colour is black, frequently with a shade of grey; its lustre is resinous; it is soft and brittle, and has a specific gravity of about 1.25. It softens, cakes, and burns brightly, and leaves, when burnt, a small residue of ashes. It contains a proportion of bitumen, varying however, so much as from 24 to 40, with from 53 to 70 of carbon, and 2 or 3 of earthy matter and oxide of iron. Foliated coal approaches to the slaty, being distinguished by its fracture and its greater lustre; it is softer, and appears to contain more bitumen. Columnar, coal so named from occurring in columnar distinct concretions, is more rare. Cannel coal is distinguished by its smooth conchoidal fracture; it has a resinous lustre and black colour, and burns at first with a clear light, which, however, soon ceases. It contains about 75 of carbon, with 22 of bitumen, and 3 of foreign matter. Pitch coal has a smooth conchoidal fracture, with resinous lustre, and a deep black colour; from the closeness of its texture it takes a polish, and forms what is named Jet.

Brown Coal occurs massive, having an imperfect conchoidal fracture, sometimes fibrous and woody, soft and light; it burns with a blue flame, and gives a smell like bituminous wood; it occurs with some of the following varieties, in alluvial land: it contains little bitumen. Connected with this is what is named Earthy Bituminous Wood, or Earthy Coal, which is found of a loose consistence, nearly earthy, dull, of a blackish brown colour, light and soft. The last of the series, or that most evidently of vegetable origin, is Bituminous Wood. The ligneous texture is distinctly marked, and even the external shape of the branches and stems of trees, and the annual rings of the wood, are preserved, so as to resemble wood imperfectly charred. Its colour is brown, of different shades; it is opaque; with little lustre; has little density or hardness, and is so light as nearly to float on water. It burns with a clear flame, and with a bituminous odour, and leaves a small quantity of white ashes.

Coal, excluding the anthracite or blind coal, has been supposed to be of vegetable origin. There is a gradation from bituminated wood; in some varieties the structure, and even the remains of plants, are apparent; and its chemical composition agrees with that of vegetable matter. It is difficult, however, to determine in what manner it has been formed, or by what operations the vegetable matter from which it is originated, has been so far modified as to have assumed the properties under which it exists. In one geological system, it is maintained, that it derives its origin from vegetable matter which has been exposed under compression to subterranean heat; in another it is supposed to have been formed from vegetable matter suffering slow decomposition under water, or at least in a state of humidity, by which its oxygen and hydrogen had been in a great measure withdrawn, and its carbonaceous base left predominant. The merits of either supposition must rest on those of the more general systems with which they are connected. It has even been doubted whether the common or black coal is of vegetable origin; and Mr Jameson maintains the opinion, that, like blind coal, it is an original mineral deposite.

The bituminous part of coal is separated from the carbonaceous part by the application of heat. We perceive this separation in its combustion in a common fire; the coal, when first kindled, swelling and softening, exhaling a kind of bitumen, and burning with smoke and light; while, after a certain period, these appearances cease, and it burns only with a red light. The separation is effected more completely by the application of heat in close vessels; the bitumen is melted out, and there are disengaged ammonia, partly in the state of carbonate, with empyreumatic oil, and a gas, a variety of carburetted hydrogen, approaching to olefiant gas, though not altogether the same, which burns with a bright flame; it is often mixed with carbonic acid, and sulphuretted hydrogen; the carbonaceous matter is in a great measure left, forming Coak. In the soot of coal there is generally a considerable proportion of sulphate of ammonia, and carbonate of ammonia is one of the products of its distillation. The origin of the ammonia is not very obvious.

This decomposition of coal by heat has been carried on on a large scale, with a view to collect the products; the bituminous matter, or mineral tar, being applied to the uses for which vegetable tar and pitch are employed, and the coaked coal being used in the smelting of metallic ores, and for other purposes. The elastic fluid is extensively applied to afford by its combustion artificial light, and has the important advantages of affording a steady, uniform, and easily regulated light, and of being economical when the process is conducted on a large scale. This has been already considered.

SECT. III.

HYDRO-CARBONACEOUS MINERALS.

To this genus belong principally the liquid bitumens.

Of these Naphtha is the purest. It is very light, its specific gravity being usually about .8; of a pale yellow green colour, transparent, thin and liquid, odoriferous, volatile, and inflammable, and in burning is entirely consumed, emitting a smoke more or less dense. According to T. Saussure, it is a carburetted hydrogen, containing more carbon than olefiant gas. The proportions are, carbon 87.21, hydrogen 12.79 *.

Petroleum, or Mineral Tar, is semi-liquid, often of a thicker consistence, tenacious, semi-transparent, of a reddish brown colour, and rather fœtid odour. Mineral Pitch, or Maltha, is solid, but soft, has a degree of tena-

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* Annals of Philosophy, vol. x. p. 127.

city, and a strong bituminous smell. Its colour is black, its lustre highly resinous. It is sometimes elastic, forming what has been named the Elastic Bitumen. ASPHALTUM is the last of the series, and forms the connection with pitch coal. It is of a black colour, and resinous lustre, without transparency; its fracture is conchoidal; it is light, and has a bituminous smell when rubbed or heated. It melts easily, takes fire, and burns without leaving any ashes.

Through all these substances there is a gradation; naphtha, by inspissation, becoming petroleum, and this, by the same operation, passing into asphaltum; and even the different specimens of these are frequently found in the same situation. They also agree in their chemical characters, are inflammable, insoluble in water and in alkohol, but combine with fixed and essential oils, and are partially soluble in ether. They are not dissolved by the alkalis, and are decomposed by the more powerful acids. There exists, perhaps, a specific distinction between naphtha and the others. It is often contaminated with petroleum, and then exhibits the gradation into the series. But Saussure found, that when pure, it does not become inspissated, nor darker in its colour from exposure to the air, and it is completely soluble in pure alkohol: it combines in all proportions with ether, and with essential and expressed oils, and dissolves camphor, but not resins.

FOSSIL RESIN occurs in beds of clay in round masses of a brownish colour, semi-transparent, with resinous lustre; it is fusible and inflammable. RESIN-ASPHALT is another substance of resinous lustre and appearance, but opaque; it softens when heated, gives a fragrant odour, and burns with bright flame. It is a compound of resin and asphaltum, and is found in brown coal.

AMBER is placed among the bitumens. It is of a yellow colour, pale or deep, with a shining lustre, and a transparency more or less perfect; its fracture is conchoidal; it is brittle, and has a specific gravity of 1.08. It is inodorous, unless when heated, and is insipid. When rubbed it becomes strongly electrical. It occurs in fragments, or in masses, in layers of bituminated wood, or under sand on the sea shore. No satisfactory theory has been given of its origin. It often contains very perfect organic remains, —a proof of its having once been fluid. It approaches to the resins in chemical properties, but presents some peculiarities, especially in affording a peculiar acid, when decomposed by heat.

When exposed to heat, it softens and swells; an acidulous liquor passes over with an empyreumatic oil; this is succeeded by a concrete acid, which condenses in flakes or needles; a black resinous-like substance forms the residuum. When heated in contact with the air, it inflames, burns with much smoke, and with a strong bituminous smell, and leaves little residue.

Water exerts no action on amber. Alkohol acts on it weakly, acquires colour and a degree of tenacity. The alkalis in solution dissolve it, and form a kind of soap. The more powerful acids change it into a species of resin, and ultimately into the product named Artificial Tannin.

One property in which it differs from the resins, is that of not being dissolved by expressed or essential oils; it becomes soluble by being roasted gently, and solutions of this kind are used as varnishes.

The empyreumatic oil obtained from the decomposition of amber by heat is thick, and of a dark colour: by distilling it repeatedly, with the addition of a little water, it becomes thinner and of a lighter colour. It retains a fœtid smell: is volatile and inflammable: insoluble in water, and imperfectly soluble in alkohol. It combines imperfectly with the alkalis.

The acid obtained by the same decomposition, Succinic Acid, is possessed of properties which sufficiently distinguish it. When freed from the empyreumatic oil which adheres to it, by repeated solution and crystallization, with filtration through charcoal powder, or by combining it with potash, decomposing the salt thus formed, by acetate of lead, and then decomposing the succinate of lead by sulphuric acid, it is obtained in four-sided rhomboidal plates, which are white; their taste is sour, and they redden infusion of litmus; they require twenty-four parts of cold water for their solution, but are abundantly soluble in hot water; they are also soluble in alkohol. This acid is volatile and inflammable. It is decomposed by heat, and affords products which shew that carbon, hydrogen, and oxygen, are its elements. Berzelius has inferred, that the proportions are 47.4 of carbon, 48.80 of oxygen, 4.52 of hydrogen. Considering it according to the theory I have illustrated, the relation of the oxygen to the carbon, is that constituting carbonic oxide, that of hydrogen is that between the first and second proportions, which it usually observes.

Succinic acid combines with the alkalis, earths, and metallic oxides, but few of these combinations present any important results. They were examined by Bergman. Succinate of potash crystallizes in tetraedral prisms, which are easily soluble in water. Succinate of soda crystallizes in nearly the same form. Succinate of ammonia appears under the form of needle-shaped crystals, having a saline and bitter taste, and volatile. Succinate of barytes is of very sparing solubility in water. Succinate of lime affords long spear-shaped crystals permanent in the air, and not easily dissolved even by boiling water. Succinate of magnesia does not crystallize, but by evaporation forms a viscid mass. Succinate of alumina is of sparing solubility, and hence succinic acid affords a test to distinguish between alumina and magnesia, succinate of ammonia causing a precipitation from the salts of the former earth, but not from those of the latter.

The metallic succinates in general are soluble and crystallizable. Succinate of iron is insoluble, and from this property succinic acid has been employed as a test of this metal, and as a re-agent by which substances may be freed from it, succinate of potash or ammonia being added to any solution containing iron, and the succinate of iron being precipitated.

Mellite or Honey-stone has been placed among the bitumens, with which it has some relations. It is found in the layers of bituminated wood. In its external appearance it has some resemblance to amber: is of a honey yellow colour, whence its name; is more or less transparent, and has the property of double refraction; its lustre is intermediate between vitreous and resinous; its surface is smooth, its fracture conchoidal: it is brittle, and softer than amber; has a specific gravity of 1.6. It occurs crystallized in octaedrons, dodecaedrons, or four-sided prisms acuminated by four planes. When heated in contact with the air, it burns without becoming sensibly charred, and leaves a white matter, which produces a slight effervescence with acids. Klaproth discovered that it consists of a peculiar acid, combined with alumina *, which was confirmed by Vauquelin, who also found in it portions of silica and lime †.

Mellite acid may be extracted from the honey-stone, by boiling water on it; the alumina is precipitated, and the acid dissolved can be obtained by evaporation in a mass, which, when subjected to the action of alkohol, to separate some earthy matter, may be crystallized. Or it may be procured by adding the crystals of mellite in powder to a solution of carbonate of potash: the mellitic acid combines with the alkali, and on adding to the filtered liquor a lit-

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* Analytical Essays, vol. ii. p. 89.

† Nicholson's Journal, 4to, vol. iv. p. 515.

tle nitric acid, the mellitic acid is deposited in a few hours, crystallized in short prisms. It has a yellowish tinge, and a slight acid taste, with bitterness. It is sparingly soluble in water. Exposed to heat it swells, emits a dense smoke, is charred, and leaves a light coal. It affords the usual products of the decomposition of vegetable substances, and from the large quantity of carbonic acid it affords, it appears, as Vauquelin remarked, to contain a large proportion of oxygen. It is not converted into oxalic acid by the agency of nitric acid.

The compounds of mellitic acid, with the different salifiable bases, have been only imperfectly examined. Mellate of potash crystallizes in prisms: Mellate of soda crystallizes in cubes, and in plates. The acid neutralized by ammonia, gives transparent six-sided prisms, which become opaque from exposure to the air. Added to the watery solution of barytes, strontites, or lime, a precipitate of a white powder falls down, indicating the formation of an insoluble salt. If added, however, to muriate of barytes, it gives a precipitate in needle-like crystals, and to sulphate of lime, a granulated crystalline precipitate. With solution of silver it gives a white silky precipitate; with nitric solution of lead, a very heavy white precipitate; with that of mercury, a white precipitate, and with that of iron, a yellow precipitate.

Vauquelin has observed, that this acid is in many of its properties similar to the oxalic. The principal differences are, that the precipitate which mellitic acid causes in the solution of sulphate of lime, is less speedily manifested, and is crystalline instead of being pulverulent, like that formed by the super-oxalate of potash; and that supermellate of potash, added to a solution of sulphate of alumina, gave an abundant flocculent precipitate, while super-oxalate of potash caused no precipitation.

CHAP. VI.

OF THE CHEMICAL ANALYSIS OF MINERALS.

The processes which are followed in the investigation of the composition of minerals, are so various, and require to be adapted so much to the composition of the substances submitted to analysis, that a few general rules only can be delivered with regard to them. The minute knowledge of this branch of chemistry, is to be acquired from the study of the particular analyses, executed by those who have bestowed the greatest attention on such investigations. Margraaf and Bergman introduced the methods first employed; Klaproth and Vauquelin greatly extended them; and they receive constant improvements from the chemists of the present time.

In the operation of mineral analysis, the utmost attention is requisite in weighing the substances and their products, in selecting proper specimens of the substance to be analysed, and in employing re-agents perfectly pure.

In proceeding to the analysis of a mineral, some judgement must be formed of its nature, so as to suggest the methods to which it is to be subjected; and in particular, we ascertain from its obvious qualities, to what order it belongs, whether saline, inflammable, earthy, or metallic.

If it be Saline, and hence soluble in water, the general process is comparatively easy.

A quantity of it carefully weighed, is submitted to lixiviation with water, by which it is either entirely dissolved, or the soluble part is freed from the insoluble matter, and the proportion of these to each other is determined by weighing the latter when dry. The solution is filtered, and we determine by its effect on the colours of litmus, and turmeric, whether it has an excess of acid or of alkali, or is in the neutral state.

It may, for more minute examination, be evaporated so far, that on cooling, the dissolved salt may be obtained crystallized, and from the figure of the crystals, and other properties, the nature of the salt may be determined. If more than one salt be present, the difference in the form of the crystals will in general point this out, where they do not from the influence of mutual affinity form one uniform crystallized mass. By cooling the liquor at different stages of the evaporation, the separation by crystallization of different salts may also be effected, or by evaporating the whole to dryness, and treating the dry mass successively with small portions of water, the separation may be obtained more or less perfectly. The examination may farther be aided by the application of precipitants; alkohol is in particular useful in this respect. If added to the solution, it precipitates the alkaline and earthy sulphates, even when the solution is diluted; when more concentrated, it throws down the alkaline muriates; and by being thus added successively in different quantities, and to the solution in different states of dilution, we are enabled if two or more salts are mixed to facilitate their separation; as will be more fully stated under the history of mineral waters, to the analysis of which this re-agent is principally applied.

We farther determine by re-agents the nature of the saline matter. Salts containing sulphuric acid, give a precipitate with muriate of barytes insoluble in water, and not affected by a dilute acid. Carbonates give a precipitate with the same re-agent insoluble in water, but which is dissolved with effervescence by dilute acids. Muriates give an insoluble precipitate with nitrate of silver. Nitrates are not affected by either of these re-agents. From the quantities of the precipitate obtained by these methods, the quantity of acid is indicated, according to the known composition of sulphate or carbonate of barytes, or muriate of silver; and from this again the quantity of neutral salt is determined, according to the tables of the composition of salts, when it is discovered with what base the acid is combined. The nature of the base is in general best determined, from the entire salt having been procured by the method of evaporation, or sometimes it is discovered by other modes. Ammonia is detected by its smell on the addition of lime; and potash or soda may be discovered by the evaporation of the liquor remaining after the precipitation by muriate of barytes or nitrate of silver, muriate or nitrate of potash or soda being obtained. These bases may be farther discriminated, by tartaric acid forming with potash, when the acid is in excess, a salt of sparing solubility, while with soda it forms one much more soluble, and by the solution of muriate of platina forming a precipitate with the salts of potash, and not with the salts of soda. The soluble earthy salts may be discovered by the solution giving a precipitate on the addition of potash; the precipitate, if magnesian, is distinguished by not being dissolved by an excess of potash; if argillaceous, by being dissolved by this addition; and if calcareous, it is discovered by its solubility in water to a certain extent, so as to communicate a styptic taste, and the power of changing the vegetable blue colours to a green; and by a similar precipitate not being thrown down by ammonia. The presence of any soluble metallic salt is discovered by the colour, the acrid metallic taste, and the precipitate which is thrown down, generally of a dark colour, by prussiate of potash, infusion of galls, or hydro-sulphuret of potash. If both earthy and metallic salts are present, when the solution has ceased to give a precipitate with prussiate of potash, it will afford a farther precipitate on the addition of pure potash, or its carbonate.

The investigation of the composition of an EARTHY MINERAL presents greater difficulties. Vauquelin has given an account of the general processes to be followed *, of which the following is an abstract, with a few additions with regard to some peculiar methods.

As these minerals have generally a considerable degree of cohesion, which resists the action of solvents on their constituent principles, it is necessary that this should be overcome. Pulverization is therefore a necessary preliminary operation. The mineral is often not easily reduced to a powder sufficiently fine; it is therefore raised to a red heat in a crucible, and while hot is plunged into cold water, by which it is split, and rendered more friable; and if necessary, this is repeated on its fragments two or three times. It is then pulverized in a mortar of agate, or, if very hard, its fragments are first broken in a steel mortar, polished and nearly cylindrical, the pestle fitting it exactly, that the fragments may not be struck out. They are then reduced to powder in a mortar of agate or flint; when brought to a coarse powder, a certain quantity, 100 grains for example, is weighed, and is triturated in small portions, not exceeding ten grains, until it is reduced to a fine and smooth powder. Minerals which are very hard wear down a portion of the mortar during the trituration, the earth of which, of course, mingles with the powder; to guard against the fallacy from this, it is necessary that the quantity pulverized should have been carefully weighed, and care having been taken that no part of the powder is lost, it is weighed at the end; any increase of weight shews what has been added to it from the substance of the

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* Annales de Chimie, tom. xxx. p. 66.

mortar: the greater part of this from a mortar of flint or agate will be siliceous earth, though, to attain more precision, its nature may be determined by a previous analysis; and at the end of the analysis it must be taken into view, in estimating the ingredients and their proportions, and subtracted from them. A crucible of platina ought to be used in exposing the mineral to heat: it must have a cover, and a spathula of the same metal; the evaporating dishes may be made of glass, porcelain, or silver.

The mineral having been prepared by trituration, is now to be submitted to analysis. There are nine primary earths, but not more than four of these, silica, alumina, magnesia, and lime, are usually found, and with these are combined some metallic oxides, principally those of iron, manganese, nickel, chrome, and copper.

The general mode of analysis, where there is no reason to suppose in a mineral the presence of an acid, but that it is composed of earths united with each other, or with a metallic oxide, is first to expose it to heat with potash: 100 grains of the stone in fine powder, with three times its weight of the pure alkali, being heated in a crucible of silver, adding at first a little water, that the potash may act more equally on every part of the earthy matter, applying the heat gently, and stirring constantly: when the ebullition has ceased, the heat is to be raised to redness, and the mixture exposed to this for three quarters of an hour. From the appearances presented during this operation, some conjectures may be formed with regard to the nature of the mineral. If the mixture pass into perfect fusion, it may be concluded that it is chiefly siliceous; if it remain thick and opaque, the other earths predominate; if it remain in the state of a grumuous powder, the volume having increased considerably, it may be inferred to be chiefly argillaceous; if it has a dull green or brownish colour, oxide of iron is present; a clear grass-green gives a proof of the presence of manganese, particularly if this is communicated to water; a greenish yellow colour indicates chrome.

The crucible being taken from the fire, and cleaned, is placed in a capsule of porcelain, which is filled with water, this being poured off repeatedly, until the matter is entirely detached. The water dissolves a portion of the compound of potash with silica and alumina, if these earths existed in the stone, and would dissolve the whole of it, if added in sufficient quantity.

The detached matter is dissolved in muriatic acid; at the commencement of the solution a precipitation takes place of a flocculent matter: then an effervescence happens from the decomposition of the alkaline carbonate, formed after and during the fusion; and the precipitate is re-dissolved. Lastly, the portion of matter not dissolved by the water, which had remained in the form of powder, is dissolved, this not being attended with effervescence if it consist of silica and alumina, while there is an effervescence more or less if it consist of lime. If the liquor assume a purplish red colour by the solution of the matter in the acid, it is a farther proof of the presence of manganese; an orange-red colour indicates iron, and a golden-yellow colour, chrome: if free from colour, it either contains no metallic oxide, or only a small portion.

If the solution of the matter is complete, it is evaporated to dryness in a vessel of porcelain covered with paper: if any part has remained undissolved, it is to be again subjected to fusion with potash, and the same subsequent treatment, or it is to be put aside, and deducted from the weight of the fossil employed. When the evaporation is nearly finished, the liquor becomes gelatinous; it must then be stirred with a glass rod, to facilitate the disengagement of the last portions of acid and water, and to render the exsiccation uniform, as otherwise there is the risk of there remaining with the silica a portion of alumina from which the acid has been expelled, and with alumina a portion of silica retained in solution by the acid not sufficiently dissipated.

When by a gentle heat the matter is reduced to a powder almost dry, it is to be diffused in a large quantity of distilled water, and heated gently; it is poured on a filtre, the powder collected is washed with water, until the last portions give no precipitate with solution of silver. This powder is SILICA ; it is to be exposed to a red heat in a platina crucible, and weighed while warm. It ought to form a fine white powder, insoluble in acids; if coloured, it contains traces of a metallic oxide. To remove this, the powder is boiled with an acid, and washed and dried ; and the liquor poured off must be added to that which holds dissolved the other principles.

This solution must be evaporated to about an English pint, and precipitated by a solution of carbonate of potash, boiling it for a few moments, that nothing may remain suspended. The precipitate is collected, is diffused in a little water, and poured on a filtre. When the water has run through, the filtre is placed on some folds of bibulous paper, that the matter may acquire a consistence ; it is then boiled with a solution of potash in a capsule of porcelain. If it has contained alumina or glucine, they will be dissolved ; the other earths and metallic oxides remain undissolved.

The solution of alumina in the potash is to be supersaturated by an acid, as much acid being added as re-dissolves any precipitate ; carbonate of ammonia is then added in excess ; any alumina will thus be precipitated, while glucine, if present, will remain completely dissolved. The precipitated ALUMINA is to be collected on a filtre, washed with distilled water, calcined, and weighed. It is proved to be alumina, by dissolving it in sulphuric acid, and adding to the solution a sufficient quantity of sulphate of potash to convert it into alum. If GLUCINE remain in the residual liquor, it will fall down on boiling it for some time, so as to dissipate the excess of ammonia. After being washed and calcined, it is to be weighed.

The matter remaining undissolved by the solution of potash, may consist of lime, magnesia, and metallic oxides. It is submitted to the action of sulphuric acid considerably diluted : the solution is evaporated to dryness, so as to dissipate any excess of acid, and the solid matter is diffused in a little water. The metallic sulphates and the sulphate of magnesia will be dissolved. The sulphate of lime will remain undissolved ; by calcining it at a red heat, its weight will give the quantity of LIME.

The substances retained in solution with the sulphuric acid, may be magnesia and oxides of iron, manganese, chrome, and nickel. To separate them, the solution is to be diluted with a large quantity of water, a slight excess of acid added to it, and then a solution of carbonate of potash saturated with carbonic acid is to be poured in : the oxides of iron, chrome, and nickel, will be precipitated ; the magnesia and oxide of manganese will remain in solution with the potash and carbonic acid. To separate the two latter, hydro-sulphuret of potash, well saturated with sulphuretted hydrogen, is to be added ; the manganese will be precipitated in the state of hydro-sulphuret. The MAGNESIA remains dissolved ; it is precipitated by adding pure potash, and its weight is estimated after it is dried at a red heat. To obtain the weight of the OXIDE OF MANGANESE, its precipitate must be calcined with the admission of the air to expel the sulphuretted hydrogen.

There remain the oxides of chrome, iron, and nickel, if they are all present in the precipitate thrown down by the carbonate of potash. To separate them, the precipitate is boiled in successive portions of nitric acid, to bring to the state of acid the oxide of chrome ; it is then heated for a few moments with potash, and is diffused in water, the liquor is poured off, and the undissolved matter is washed with water, which is added to the other : in this solution the chromic acid exists combined with the potash; muriatic acid is added to it, so as to be in excess; it is evaporated until it assumes a green colour, from the reduction of the chromic acid to the state of oxide; the precipitate then thrown down by potash, gives, when dried, the quantity of OXIDE OF CHROME.

The undissolved matter of the preceding experiment may consist of oxides of iron and nickel. It is dissolved in muriatic acid, and ammonia is added to the solution in excess: it dissolves oxide of nickel. The OXIDE OF IRON is precipitated, and its weight is estimated when it is dried. The OXIDE OF NICKEL may be obtained by evaporation and dissipation of the ammonia.

When the different constituent principles of a fossil have thus been procured separate, their weight ought to be equal to the weight of the fossil itself, at least with not a greater difference than two or three hundredths from loss. If the *deficit* exceed this, the analysis ought to be repeated; and if the result is still the same, it may be concluded that the mineral contains some principle, either volatile, or soluble in water, which must be sought for.

Being broken into very small fragments, it is first to be exposed to a strong red heat in a retort of porcelain, to which a receiver is adapted. If it contain water, or any other volatile substance, this will be collected in the receiver. If it sustain no loss by this operation, or a loss not equivalent to that indicated by the analysis, it is probable that it contains some substance soluble in water.

Potash existing in a number of stones, may be supposed with probability to be present. To discover this, the fossil reduced to powder is to be boiled with six or seven times its weight of sulphuric acid in successive portions: the heat is to be raised toward the end of the operation, to drive off the excess of acid, avoiding such a degree of it as would decompose the salts formed. The matter is then diffused in boiling water; it is washed until the water pass off tasteless, and the liquor being poured off is evaporated to dryness, to separate more completely any excess of acid. The dry matter is diffused in water, with which it is made to boil for a few minutes; the liquor is then filtrated, and is evaporated to that degree which shall appear best adapted to crystallization. If the mineral has contained both alumina and potash, alum will be obtained: if the alumina is not in sufficient quantity to form the whole quantity of alum which the potash would form, there must be added a certain quantity of it dissolved in sulphuric acid. The alum frequently does not crystallize for several days, or even weeks. Often the quantity of alumina is so large, and of course the quantity of sulphate of alumina formed so considerable, that it prevents, by the density it gives to the liquid when it is evaporated, the crystallization of the alum. The quantity of Potash obtained by these methods, may be estimated by the quantity of alum, being equal to the tenth of that quantity; and to obtain perfect certainty with regard to the presence of potash, the alum dissolved in water may be decomposed by water of barytes, and the potash which will remain in solution may be obtained by evaporation. By combining it with nitric acid, it will be distinguished by affording crystals of nitre. Or its presence may be indicated by the orange precipitate it gives with muriate of platina.

If no alum is procured, the loss must be looked for in some other principle soluble in water. This will probably be Soda; it may be discovered by decomposing by ammonia, the solution obtained in treating the stone with sulphuric acid, and in calcining the saline matter procured by its evaporation: the sulphate of ammonia will be volatilized, and that of soda will remain.

It may happen that the fossil is not sufficiently acted on by sulphuric acid, and that therefore these methods cannot be employed: it must then be treated by the general method already described, only employing soda instead of potash;

the product being diffused in water, the liquor is saturated with sulphuric acid, and evaporated to dryness: it is dissolved in water to separate the silica, and again evaporated; a portion of sulphate of soda first crystallizes, and on a second evaporation alum is obtained, if the fossil has contained alumina and potash.

Stones which are not readily acted on by potash, or soda, and this is the case with these which are composed chiefly of alumina, may be exposed to heat with calcined borax. This method has been employed by Chenevix *.

Another method of analysis for those minerals containing the alkalis, was invented by Rose. It consists in fusing the mineral in powder with four times its weight of nitrate of barytes, in a silver or porcelain crucible; and dissolving the mass after it is cold in dilute muriatic acid. As much sulphuric acid is added as precipitates the barytes, and expels the muriatic acid; and the liquid is evaporated to dryness. The dry mass is digested in water, and the undissolved matter, consisting of sulphate of barytes, and any silica present, is collected. The filtered solution is saturated by carbonate of ammonia, the earthy and metallic bases are precipitated, and sulphate of ammonia, with any alkaline sulphate, remain in solution. The liquor is evaporated to dryness, and the sulphate of ammonia is dissipated by heat; any sulphate of potash and soda present remains, and may be crystallized; or it may be decomposed by acetate of barytes, and the alkaline acetate decomposed by a red heat, will afford the alkaline carbonate in a pure form. According to Gmelin, carbonate of barytes may be substituted for nitrate of barytes in this process, with equal advantage.

Some minerals contain fluoric acid. It is detected by the erosion or opacity produced in the upper part of a retort, in which the mineral in powder is heated with sul-

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* Philosophical Transactions, 1802.

phuric acid; and this indication is rendered more decisive by the deposite produced when the air expelled comes in contact with water.

Those fossils in which earths are combined with acids, forming compounds not soluble in water, require a different mode of analysis. The earthy carbonates are analysed by calcination by heat with or without charcoal, or by solution in dilute muriatic or nitric acid, estimating the quantity of carbonic acid disengaged by collecting it, and discovering the base by the nature of the salt obtained by evaporation, or by precipitation by re-agents, and estimating by the same modes the quantities of them. Earthy sulphates may be decomposed by boiling with carbonate of potash for a considerable time; the sulphuric acid is attracted by the potash, and its quantity may be estimated by precipitating by barytes; the carbonic acid is attracted by the earthy base, and the carbonate thus obtained may be decomposed in the same manner as a native carbonate, or the quantity of earth which it contains may be estimated from its weight. Phosphate of lime may be dissolved in diluted nitric acid with the aid of heat; the lime may be precipitated by sulphuric or oxalic acid; the phosphoric acid remaining dissolved may be obtained solid by evaporation, or its quantity may be estimated by precipitating it by acetate of lead, 100 grains of phosphate of lead containing 22.5 of acid. Fluate of lime may be decomposed by sulphuric acid aided by heat; the fluoric acid gas will be discovered by its power of eroding glass, and may be collected over quicksilver; the quantity of lime may be estimated from that of calcined sulphate procured.

The force of aggregation in Metallic Minerals being usually less strong than in the Earthy Fossils, they admit more easily of analysis in the humid way. Their composition can also be ascertained in the dry way by expelling by heat, either alone or with the aid of other affinities, the mineralizing substance, and reducing the metallic matter to the metallic state.

Previous to the peculiar processes of either method, it is necessary to select proper specimens of the ore, and to free it from the adhering stony matter. This can often be struck off, or where it is more intimately blended, the whole may be reduced to powder, and advantage taken of their difference in specific gravity, to separate them by washing with water. Where the ore is to be analysed with a view to ascertain its value in the quantity of metal it affords, it is also necessary to attend to the circumstance, that from the same mineral vein it is liable to vary in richness; and to form a just estimate, therefore, equal portions of the richest, the poorest, and that of medium value, are submitted to analysis.

The general process in the dry way, after having selected the ore, and reduced it to powder, is to calcine it to expel the sulphur or other volatile matter, the calcination being performed at a low red heat in an earthen vessel, to which a loose cover is adapted to prevent any of the matter being thrown out by decrepitation; the operation is also performed in an earthen retort and receiver, where the sulphur is to be collected that its quantity may be estimated, though in this way its entire expulsion from the metallic matter is much more difficult. The residual matter in either case, being weighed to ascertain the loss of weight that has been sustained, is mixed with three times its weight of black flux, and exposed in a crucible to a heat sufficiently intense for its reduction and fusion, the carbonaceous matter of the flux effecting this reduction, while its alkali promotes the separation and subsidence of the metallic matter by its liquefaction, and at the same time by vitrifying any earthy matter present. Sometimes other fluxes are necessary to produce the entire separation, composed generally, along with charcoal, of borax, with the addition of pounded glass, or of lime. The metallic matter, when the operation is well performed, is collected in a button at the bottom of the crucible; its nature is obvious from its properties, or if it is found to be an alloy, it is submitted to operations conducted in the humid way, by which the metals composing it are separated by precipitation, or by their particular tests.

In submitting an ore to analysis in the humid way, the general process is to digest it, previously reduced to powder, in different acids. Sulphur, if present, is precipitated, or is partly converted into sulphuric acid. Or the sulphur is previously dissipated by roasting, a step in general necessary where it is present in large proportion, as it impedes the action of the acid on the ore. The residual matter is then submitted to the action of the different acids, these being often applied successively, so that different metals, if present, are separated by their proper solvents. The solution affords by evaporation the metallic salts it contains, or each metal is discovered in the solution by its proper test; it is also precipitated by the alkalis or other re-agents, and the precipitate is reduced by exposure to heat with a flux to the metallic state; or sometimes it is thrown down at once in the metallic form, by another metal having a stronger attraction to oxygen. The processes requisite to be adapted to the different ores are so numerous and complicated, that scarcely any general account can be given of them that would be of any utility. They were minutely given by Bergman, to whose Dissertation, (Chemical Essays, vol. ii.), to the second volume of Kirwan's Mineralogy, and the Analytical Essays of Klaproth, I refer.

INFLAMMABLE MINERALS are easily recognized from their external properties, and their nature can be more exactly determined by the products of their combustion. The principal subjects of analysis among the minerals of this order, are the carbonaceous minerals—the Bitumens and Coals, the object being chiefly to determine the proportion of carbonaceous matter which they contain. The quantity of bitumen in coals is found by the loss of weight they suffer in distillation, the residual coak being chiefly carbonaceous matter; it contains at least, in addition to this, only the small quantity of earthy and metallic matter usually present, and this remains after the perfect combustion of the coak, so that its quantity can be determined. Mr Kirwan, in his analysis of coals, with the view to determine the proportion of carbonaceous matter, employed also the method of deflagration, a given weight of the coal in coarse powder being projected in small quantities on nitre in fusion, the quantity of carbon being inferred to be proportional to the extent to which the nitre is alkalised, —a method, however, which cannot be accurate.

CHAP. VI.

MINERAL WATERS.

Mineral Waters being complicated, and diversified in their composition, cannot be strictly placed under any of the established classes of chemical arrangement. But their history may with propriety follow that of the substances which belong to the mineral kingdom, as it is of combinations of these that they chiefly consist.

All waters, rain water excepted, might be named Mineral, as they all contain a slight impregnation of earthy or metallic matter. But the term is restricted to those in which the impregnation is so considerable, as to communicate taste or flavour, or the power of acting in a peculiar manner on the animal system.

The substances contained in mineral waters are very numerous. The principal are carbonic acid, sulphuretted hydrogen, sulphurous acid, carbonates, sulphates, and muriates of soda, lime, and magnesia, and carbonate and sulphate of iron. From the predominance of certain of these ingredients, mineral waters may be characterized; they have thus been divided into four classes. 1st, Those in which carbonic acid is predominant, and which have usually been named Acidulous; 2d, The Sulphureous, the principal ingredient of which is sulphuretted hydrogen; 3d, The Chalybeate, or those having iron for their chief constituent; and, 4th, The Saline, in which various neutral salts are dissolved. This affords the most convenient arrangement under which they may be considered.

I. Carbonated Waters.—Mineral waters of this class, or those in which carbonic acid is predominant, generally contain portions of saline or earthy matter, most commonly carbonates of lime and magnesia, and sometimes of soda; but the carbonic acid in excess communicates to the water its most characteristic qualities. These waters sparkle when poured into a glass, and have an acidulous pungent taste; and they lose these qualities by exposure for a short time to the atmosphere. The quantity of gas contained is very variable: it must in general be inferior to the volume of the water, and can be superior to this, indeed, only when its condensation is promoted by the saline ingredients contained in the mineral water. The tests by which carbonic acid in a free state, or not combined with any base, is discovered, are sufficiently precise. 1st, The infusion of litmus is reddened, when the quantity of gas amounts to one-sixteenth of the bulk of the water. To render the test decisive, the redness should not be permanent, but should disappear after exposure to the air for some time, and be capable of successively disappearing and being produced by fresh additions of the water; it is thus distinguished from the more permanent redness given by other acids. 2dly, Lime-water renders the mineral water turbid, and the precipitate, to the formation of which this is owing, is soluble in muriatic or nitric acid, so that a few drops of either of these restore the transparency. It is also restored by adding an excess of the mineral water itself. This test by lime-water confirms that of the reddening of litmus; and by the disappearance of the precipitation produced by lime-water, on the addition of a larger quantity of the mineral water, or a few drops of muriatic acid, the fallacy is guarded against, that might arise from the precipitation of the lime occasioned by the presence of any sulphate. It is still liable, however, to one fallacy: if any magnesian salt is present, it precipitates the magnesia; and this precipitate is, equally with that of carbonate of lime, dissolved by an acid. Whether magnesia is present or not, without carbonic acid, and, of course, to which of them the precipitation is owing, may be known by using pure ammonia as a test, which precipitates magnesia, but not lime. Lime-water is a very sensible test of free carbonic acid, and detects it in minute quantity by the cloudiness it produces: half a grain of carbonic acid may be discovered in 7000 grains of water.

To ascertain the quantity of carbonic acid existing in solution in any mineral water that is not combined with any base, the following process has been given by Kirwan. A small retort, whose capacity is known, is to be filled with two-thirds of its contents of the water to be examined, its extremity being placed under a jar filled with mercury, and divided into tenths of a cubic inch. The water is to be heated, and kept boiling for a quarter of an hour. To the air which has been expelled, and which is collected in the jar, a small quantity of solution of potash is to be introduced, and the vessel agitated. The extent of absorption indicates the quantity of carbonic acid which the water contained; allowance also being, of course, made for the volume of air remaining in the retort; or, what is more accurate, this having been added to the air expelled.

In some mineral waters, sulphurous acid is likewise contained, which the application of the heat will expel. This, however, is very rare: when it does occur, it may be previously discovered by its smell, by permanently reddening the infusion of litmus, and by rendering colourless infusion of red rose, previously reddened by an acid. Its quantity, when it has been expelled, may be ascertained by leaving the solution of potash, to which it has been exposed, in the air for some days, and by evaporation, ascertaining the quantity of sulphate of potash it contains; or by adding to the sulphurous gas small portions of sulphuretted hydrogen, as long as any diminution of volume is produced; the mixture of these airs, by their mutual action, produces water and sulphur; and by the diminution of volume, the quantity of sulphurous acid may be discovered.

II. Sulphureous Waters.—The sulphuretted hydrogen existing in these waters is obvious from its smell. It likewise reddens the solution of litmus. Water containing it becomes turbid from exposure to the air, and deposites sulphur: a similar change is induced in it by nitrous acid, its hydrogen in both cases receiving oxygen. A solution of acetate of lead gives a very dark coloured precipitate; and mercury or silver has its surface tarnished by being immersed in it.

Various methods of estimating the quantity of sulphuretted hydrogen have been employed, particularly the separating of it by the application of heat, and receiving it over water or mercury. But the separation in this way is not complete, and the gas expelled cannot easily be collected so as to be measured, water absorbing it, and quicksilver decomposing it. The following method was proposed by Kirwan. The sulphureous water is introduced into a jar, so as to fill three-fourths of its capacity, the remaining fourth containing atmospheric air: and to this, the jar being placed inverted in water, a few cubic inches of nitrous gas are introduced : nitrous acid vapour is formed, which decomposes the sulphuretted hydrogen, and precipitates the sulphur : the addition of the nitrous gas is continued, as long as red fumes are produced by its mixture with the atmospheric air over the water, and till the water in the jar has lost its fœtid smell. The precipitation of the sulphur diffused through the water, is facilitated by heating it to 150° of Fahrenheit, a few drops of nitrous acid having been added to prevent the precipitation of the earths. It is then filtered; the excess of weight which the filtre, when dried, has gained, will shew the quantity of sulphur that has been deposited ; and from this may be estimated the quantity of sulphuretted hydrogen ; 100 cubic inches containing 34 grains of sulphur. The same precipitation of sulphur may be effected more easily by the affusion of very fuming nitrous acid on the sulphureous water ; but, according to Kirwan, the acid soon becomes too dilute to precipitate it entirely. Sometimes sulphuretted hydrogen exists in a mineral water with carbonic acid. In this case, both gases may be expelled from the water by heat, and the mixed gas may be exposed in a tube to nitrous acid, by which the sulphuretted hydrogen is decomposed.

Nitrogen gas is contained in some mineral waters. It was discovered in those of Buxton by Dr Pearson, and in those of Harrowgate by Dr Garnet. It may be expelled from the water by heat, and may be distinguished by its characters of not being absorbed by lime-water, nor affected by eudiometrical processes.

The solid ingredients of mineral waters, which constitute the two remaining classes of Saline and Chalybeate Waters, are next to be ascertained. With these ingredients, the gases already noticed are frequently combined ; but in conducting their analysis, the gaseous substance is expelled, previous to submitting the water to the action of the necessary tests. The application of these, therefore, is the same as in a water purely saline or chalybeate, in which no aerial ingredient is contained.

III. The Chalybeate Waters contain oxide of iron as their most active ingredient, generally also with portions of some of the usual saline substances which are found in mineral waters. The iron is retained in solution usually by an excess of carbonic acid, sometimes, but more rarely, by sulphuric acid. These waters have a styptic taste, and, unless when very weak, deposite a pellicle or sediment of oxide of iron on exposure to the air.

The tests by which they are distinguished, are tannin, generally under the form of infusion or tincture of galls, and the prussiate of potash. The infusion of galls affords a test of extreme delicacy. If three grains of crystallized sulphate of iron, which contain about one twenty-fourth of a grain of the metal, be dissolved in 5½ English pints of water, the solution strikes a purple colour in five minutes with one drop of the tincture; hence it discovers in water a quantity of iron, amounting only to $\frac{1}{47\cdot759}$ of its weight. A sensible tinge is even said to be produced with one grain of the sulphate dissolved in 15 gallons of water. Its delicacy is equally great when the iron is dissolved by carbonic acid. The tint of colour is varied by the presence of other salts. If the water contain an alkaline carbonate, it is violet; if neutral alkaline salts, dark purple; if earthy salts, violet; if sulphate of lime, the precipitate is at first whitish, and afterwards black; and if sulphuretted hydrogen, the tinge will be a purplish red. Mr Phillips has shewn, that carbonate of lime has a singular effect on the production of the colour. When the iron is in a low degree of oxidation, it rather heightens the colour; while, when it is at the maximum of oxidation, it diminishes it so much, that if the iron be present in very minute quantity, it may even not be capable of being detected by this test. And he has thus been enabled to explain a fact before inexplicable, and which had given rise to various opinions with regard to the waters of Bath,—that when taken immediately from the spring and while hot, they give indication of a small quantity of iron, by the test of infusion of galls, while, when they have cooled under exposure to the air, so that the iron becomes more oxidated, they appear, from the same test, to contain none, though no iron is deposited during the cooling.

By applying this test before and after ebullition, we discover whether the iron is dissolved by carbonic or by sulphuric acid; since, if the colour is not produced after ebullition, when the liquor has cooled and become clear, it is a proof that carbonic acid has been the solvent, the heat having expelled it, and the oxide been precipitated.

Prussiate of potash, or rather the triple prussiate of potash and iron in that state in which it gives no blue precipitate with an acid, has been used as a test of iron, by the blue colour it produces. Independent, however, of some sources of fallacy, from the presence of other substances, as of any free alkali which prevents the blue colour from appearing, the test itself is liable to fallacy from its composition. The triple prussiate contains a quantity of iron essential to its composition; and when an acid is evolved, this is liable to give rise to the blue precipitate, even though iron should not be contained in the mineral water, at least unless the test be well prepared. It has one advantage, that of indicating the presence of other metals, by the precipitates it forms from metallic salts.

To estimate the quantity of oxide of iron, various methods are employed. The water may be left exposed for some days to the air; the oxide of iron, passing to the maximum of oxidation, is deposited; its separation, however, is perhaps not altogether complete, especially when the water contains any saline matter. Prussiate of potash, or infusion of galls, may be employed for its precipitation: to favour their action, the water is concentrated by evaporation as far as it can be without occasioning any separation, adding previously a minute quantity of muriatic acid, to retain the oxide of iron dissolved. The prussiate of potash, or infusion of galls, is then to be added in successive portions, allowing the precipitate formed by either of them to subside, and continuing the addition as long as they produce colour; the precipitate being washed, is calcined with a red heat, and its weight gives the quantity of oxide of iron. Both methods, however, are defective. The prussiate of potash itself contains iron, and it is nearly impracticable to employ it, so as to guard completely against the fallacy arising from this. The precipitate from the infusion of galls subsides very slowly; the whole of the iron is scarcely thrown down by it, and the precipitate is liable to have a small portion of earthy matter adhering to it. Succinate of ammonia has been used as a precipitant; the oxide of iron falls down in combination with the succinic acid, and may be obtained by calcination at a red heat. The separation of the iron, however, does not succeed perfectly but from a concentrated solution; and alumina, if present, is liable to be thrown down. Benzoate of ammonia, which has been employed in a similar manner, is still less perfect. What I have found on the whole the best method, is to add to the liquor evaporated, with the previous addition of a minute portion of muriatic acid, as already described, a minute quantity of ammonia, so as to produce the slightest possible alkaline excess; if the quantity of oxide of iron is considerable, it is immediately thrown down; if it is in small proportion, it separates slowly from the liquor put aside for a day or two. Its separation may be even effected in this manner, without any previous evaporation. The precipitate is washed and converted into red oxide of iron by calcination at a red heat. If too much ammonia has been added, a little alumina or magnesia may have been also thrown down, but it is easy to obviate this to any sensible amount; and if present, they may be abstracted from the oxide by a little distilled vinegar. The oxide of iron existing in a mineral water, may in general be presumed to be the protoxide; while it is the peroxide, which is obtained by calcination; 100 of the latter are equivalent to 90 of the former.

The only other metallic oxide that has been found in mineral waters, is oxide of manganese. It was discovered combined with muriatic acid by Bergman, in some waters in Sweden; and has since been found in the waters of Lemington Priory, by Mr Lambe. It is detected by prussiate of potash giving a white, and hydro-sulphuret of ammonia a black precipitate, and by carbonate of ammonia or soda throwing down a precipitate, which becomes black when laid on a plate of iron at a red heat.

IV. The last class is that of SALINE WATERS,—those which contain saline ingredients. There are two objects in their analysis,—first to discover their presence, and secondly, to estimate their quantities.

The mineral acids, when not combined with any base, are discovered by giving a permanent red colour to vegetable infusions. These acids, uncombined, are however very seldom found. The sulphuric and muriatic, it is said, sometimes occur, with some of the earths, so that an excess of acid is present. The boracic acid has been found in some hot springs; but it must rarely be expected.

The neutral and earthy salts are the chief constituents of mineral waters. In analysing a water with a view of detecting these, it is in general necessary, first to reduce the quantity of water by evaporation,—for as the quantities of them are inconsiderable, the large quantity of water, by its solvent power, counteracts the operation of the test, by preventing the appearance of precipitates, which are abundant when the proportion of water is less. Thus, Bergman found, that a salt with a base of lime, when dissolved in fifty times its weight of water, suffers no precipitation from the addition of a fixed alkali, though this quantity of water is not by itself sufficient for the solution of the portion of lime it contains *. The water, therefore, is to be evaporated, taking care that this is not carried so far as that there shall be any separation.

Having effected this preliminary operation, the first object is to ascertain what acids exist in it in a state of combination. Sulphuric acid is often found combined both with the alkalis and earths. It is detected by muriate, nitrate, or acetate of barytes or of strontites, acetate of lead, and nitrate of mercury, the bases of which unite with it, forming insoluble compounds, which are therefore precipitated. Muriate of barytes is the most delicate of these tests: a saturated solution of it produces a sensible precipitate in water, that contains not more than $\frac{1}{190.230}$ of its weight of real sulphuric acid. Acetate of lead is much inferior, giving a precipitate only when the water contains $\frac{1}{50.990}$ of its weight; it is also inferior in accuracy. Nitrate of mercury is unfit to be employed, from the difficulty of obtaining it uniform. The barytic salts have another advantage, that they give no precipitate with muriatic acid. In using them, however, there is one fallacy to be guarded against,—that arising from the presence of any carbonate, as this decomposes the barytic salt, and a precipitate of carbonate of barytes is formed. This is discovered by the precipitate by carbonic acid disappearing on the addition of a few drops of nitric or muriatic acid, or from its not taking place when such an addition, so as to cause a sensible acidity in the water, has been previously made. These tests, it is to be remarked too, are less delicate when the sulphuric acid is not free, but saturated by combination with any base. Yet even in this case their delicacy is very great. According to Bergman, a few drops of a solution of muriate of barytes produces a cloud

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* Chemical Statics, vol. i. p. 59.

immediately in a solution of 12 grains of crystallized sulphate of soda in $5\frac{1}{2}$ English pints of water.

Muriatic acid, which, next to the sulphuric, exists most frequently in a combined state in mineral waters, is detected by nitrate of silver, a bluish white precipitate being formed by the combination of the muriatic acid with the oxide of silver. The delicacy of this test is extremely great. One grain of muriate of soda, dissolved in 42.250 of water, that is, in rather more than 5 lbs. of water, is discovered by streaks being produced in the solution on the addition of a few drops of the nitrate; this quantity of water not containing more than the $\frac{1}{108.333}$ part of its weight of real muriatic acid. The same test occasions a precipitate with sulphuric acid, though much less sensible. In using it, therefore, in the analysis of mineral waters, it is necessary to guard against this source of fallacy, by first decomposing any sulphates existing in the water by nitrate or acetate of barytes, after which the nitrate of silver may be used. It is likewise precipitated by the alkaline and earthy carbonates; and therefore, these ought to be decomposed by the previous addition of pure nitric acid; the precipitates afforded by the operation of these salts are likewise known, by being soluble in nitric acid, which the precipitate from muriatic acid is not. It is precipitated, too, by sulphuretted hydrogen; but the presence of this is always obvious, and the precipitate which it gives is of a dark colour. This test is of such delicacy and certainty, that no other need to be had recourse to, though the acetate of silver has been used.

Nitric acid seldom exists in mineral waters even in combination. It is not discoverable by any test, but only by the properties of the salts which it forms.

Carbonic acid, in combination with the alkalis or earths, is distinguished by the effervescence produced by adding sulphuric acid, and still better by muriate of barytes producing a precipitate, which is re-dissolved by nitric or muriatic acid with effervescence. The alkaline carbonates may be discovered by their power of changing the vegetable colours; rendering the blue and red colours green, and the yellow brown; even the earthy carbonates, when in considerable quantity, affect these colours, changing the red colour of brazil wood to a blue, and restoring the blue tint of litmus which has been reddened by vinegar. The earthy and metallic carbonates are discovered by being precipitated when the water is boiled, as they are retained in solution only by an excess of acid.

The preceding acids, which are those chiefly that exist in mineral waters, may be combined with the alkalis, with earths, and with certain metals. The tests of these bases are lastly to be noticed.

The earths principally existing in combination with acids in mineral waters are lime, magnesia, and alumina. They may be discovered by the following tests.

Carbonate of potash, or what is preferable, as more free from any intermixture of alumina and silica, carbonate of soda, precipitates all of them, and is a much more delicate test of their presence, than the pure alkalis. It is therefore useful, as denoting the presence of an earthy salt or salts. The nature of the precipitate is then to be determined by a farther analysis. Thus, if it be collected and heated with sulphuric acid, the insolubility of sulphate of lime will indicate that earth; the solubility of sulphate of magnesia will discriminate it; and the astringency and sweetishness of sulphate of alumina will denote its presence. The different earths may also be recognized by their respective tests.

Lime is precipitated from all its combinations by oxalic acid; and the delicacy of this test is very great. A minute portion of it discovers one grain of pure lime in 42.250 of water, by forming a cloudiness and a deposition of a precipitate in twenty-four hours. The only important fallacy to which it is liable, is where some of the mineral acids exist in the water, or are disengaged by the decomposition which the oxalic acid itself causes; they either decompose this acid, and of course destroy its combination with the lime, or they dissolve the oxalate of lime. This may in a great measure be prevented, by using not pure oxalic acid, but the oxalate of ammonia. It also precipitates magnesia; but in doing so it acts slowly, the precipitation taking place only after some hours, and not unless a large quantity of the magnesian salt exists in the mineral water; while from lime the precipitation is immediate, even when it is present in very small quantity. Any fallacy from the presence of barytes is not to be looked for, and if it were, would be easily discovered by sulphuric acid. Sulphuric acid itself has been employed as a test of lime, when it exists in combination with any other acid; but it is one much less delicate, sulphate of lime being soluble in 500 parts of water, and being much more so when there is a slight excess of acid. A negative test, useful with regard to lime, is, that pure ammonia does not precipitate it, while it precipitates both magnesia and alumina.

Magnesia is discriminated with more difficulty by any test. It is precipitated by lime-water and by water of ammonia; by the latter partially, by the former entirely. Both are liable to fallacies. Thus, with regard to lime, if any carbonate be present, the carbonic acid may be transferred to the lime, and a precipitate of carbonate of lime formed; or if a sulphate be present, there may, in like manner, be a slow precipitation of sulphate of lime. With regard to ammonia, if the magnesia exist in the mineral water in the state of carbonate, the ammonia may attract the carbonic acid, and this carbonate of ammonia reacting on any salt of lime present, may give rise to a precipitate of carbonate of lime. Both these sources of fallacy may be avoided, however, by previously decomposing any carbonate, by the addition of a little nitric acid, and removing any sulphuric acid by muriate of barytes. But a source of uncertainty attending both tests, more difficult to be avoided, is, that they precipitate alumina as well as magnesia; and although the former is seldom found in mineral waters, it may sometimes occur. It is discovered by its affording from any of its saline combinations a precipitate with carbonate of ammonia, which is not soluble in distilled vinegar, but is dissolved by boiling in a solution of potash. Succinate of ammonia too precipitates alumina, but not magnesia; and by the application of this test, the nature of the precipitate, by ammonia or by lime, may be determined. By the same methods, the presence of alumina is discovered. A convenient mode of separating magnesia where it exists with any salt, either of lime or alumina, is one introduced by Dr Wollaston, adding a solution of bi-carbonate of ammonia, which precipitates either of these earths, but not magnesia; but on farther adding to the clear liquor a solution of phosphate of soda, any magnesia present is precipitated in the state of triple phosphate of ammonia and magnesia.

Barytes has been said to be found in mineral waters, combined with muriatic acid. It is easily detected by sulphuric acid, observing the precautions already stated under lime; but its presence is rarely to be expected.

Silica has been found in some mineral waters, particularly in hot springs; not, however, in combination with any acid, but either merely dissolved by the water, by the aid of the high temperature, or by the medium of a small portion of alkali or alkaline carbonate. It is discovered by evaporating the water nearly to dryness; and adding to the residual matter nitric or sulphuric acid, and again evaporating. If the dry mass obtained by this second evaporation be dissolved in water, the siliceous earth will remain undissolved, and may be discovered by the gelatinous consistence it assumes when not quite dry; by its insolubility in every acid except the fluoric; and by vitrifying when heated, with the addition of two parts of soda, by the blow-pipe.

Lime has also been met with in its caustic state, in some hot mineral springs. A striking example of this occurs in the water of a natural hot bath, near Pisa in Tuscany. The temperature of the water is 110°, and it is so completely saturated with lime, that it deposites an incrustation of it as it cools. It contains also muriate of lime, and muriate of soda; and from the nature of the deposites, it appears also to hold combined a portion of siliceous earth. The origin of the lime is probably to be referred to the decomposition of carbonate of lime, by subterranean or volcanic heat *.

The alkalis, in a state of combination, in mineral waters, cannot be discovered by tests equally striking as those by which we discriminate the earths. But their presence is inferred, when acids are discovered in a water which are not free, and which at the same time, from the application of tests, do not appear to be in any other state of combination. The volatile alkali is seldom or never present. Potash may be distinguished from soda by the nature of the salts which it forms. The differences between some of these are sufficiently obvious to furnish tests of some nicety. Thus, the compound of soda with tartaric acid is easily soluble in water; while, when the same acid is added to a solution of potash, it forms not the soluble neutral salt, but the acidulous tartrate, which is of sparing solubility. Oxalic acid forms with soda a salt not soluble, but in comparatively a large quantity of water; while with potash, it forms a soluble salt. The solution of muriate of platina affords another test to discriminate between these alkalis; as, with the smallest quantity of potash or any of its salts, it forms an immediate precipitate, while it is not affected by soda.

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* Journal of the Royal Institution, vol. i. p. 260.

By the application of the preceding tests, the acids and the bases present in a mineral water are detected. The farther step is necessary, however, of discovering the actual ingredients; that is, the different salts which exist in solution. This has usually been effected by the process of evaporation, aided by certain analogous operations by which they are obtained in an insulated form.

A measured quantity of the mineral water is evaporated by a gentle heat, care being taken to avoid the admission of any extraneous matter. As the evaporation proceeds, different substances are precipitated successively according to their degree of solubility. The earthy carbonates, those of lime and magnesia, are first precipitated from the boiling liquor; sulphate of lime is next deposited. The evaporation is continued while any separation of this kind takes place, and until a saline pellicle begin to form at the surface; on allowing the liquor to cool, sulphate of magnesia and the alkaline neutral salts crystallize; muriate of soda crystallizes abundantly while the liquor is warm; and after these crystallizations, muriate of lime and muriate of magnesia remain in solution, forming an uncrystallizable liquor. Sometimes the whole saline matter is procured by evaporation in a solid form; and by leaving it exposed to the air, the deliquescent salts, muriate of lime and magnesia, absorb water so as to be dissolved, and the solution is poured off from the undissolved matter, which is then submitted to the agency of water, to discover its nature,—or the solid product is submitted successively to the action of small portions of water, by which the salts are separated according to their solubility, and the insoluble ingredients remain. The addition of distilled vinegar, or very dilute muriatic acid, abstracts the carbonates of magnesia and lime, leaving the sulphate of lime,—or if the proportion of this last ingredient in the insoluble residue is small; diluted alkohol acidulated with muriatic acid is applied.

The muriates formed by the action of the muriatic acid on the carbonates of lime and magnesia are dissolved, while the sulphate of lime remains altogether insoluble. Any oxide of iron that is present, remains in the insoluble residue, and is discovered by its colour and appropriate tests. Lastly, silica remains undissolved after all these operations. Its presence will be indicated by the gelatinous consistence it gives at the end of the evaporation: by repeated boiling in water, the sulphate of lime may be dissolved, and the silica remains.

The action of alkohol facilitates greatly the separation of the different ingredients. When the water is strongly impregnated with saline matter, or when it is concentrated by evaporation, those salts which are least soluble, and on which alkohol exerts little or no solvent power, are precipitated by the affusion of it in different proportions. This is very well shewn in the experiments of Boulduc, by whom this method was first employed. To eight parts of a mineral water which he had submitted to analysis, he added eight of alkohol, and found sulphate of lime to be immediately precipitated. Pouring the clear water into another vessel, five parts more of alkohol were put to it, and sulphate of soda was thrown down; and lastly, on the addition of five parts more of alkohol, muriate of soda was deposited. In general, the sulphates are most readily precipitated by this re-agent. Sulphate of lime is thrown down when present in water in the proportion of not less than 1 to 1000 parts, by alkohol, the specific gravity of which is not greater than 850. The alkaline sulphates in the same proportion may be precipitated, but slowly, by alkohol of the specific gravity of 817, and, if in a greater proportion than $\frac{1}{210}$, are readily precipitated by it when its specific gravity is even above 834. Alum and sulphate of magnesia must be in a greater proportion than $\frac{1}{240}$, to be precipitated by alkohol of this strength. Besides these, carbonates of lime and of magnesia are thrown-down, nearly as readily as sulphate of lime, if the specific gravity of the alkohol is as high as 817.

Alkohol is not less useful in the analysis by its solvent power. This application of it was made by Lavoisier. The saline matter is obtained by evaporation: eight times its weight of alkohol, of a determinate specific gravity, is added to it, and is allowed to remain over it with frequent agitation for some time; the salts most soluble in alkohol are dissolved; and by evaporation and subsequent solution in water, they may be recognized, while those which are of inferior solubility, or altogether insoluble, remain undissolved, and may be submitted first to the action of cold, and then to that of boiling water, by which the separation of different salts will be effected. The salts most soluble in alkohol, which are to be looked for in mineral waters, are muriates of magnesia, lime, alumina, and iron, and nitrates of magnesia and lime. The sulphates and carbonates are in general insoluble, or at least are of very sparing solubility. A table of the solubility of different salts in alkohol, given by Kirwan, has been inserted, vol. ii. p. 192. It is proper to remark, however, that in this application of alkohol, it does not always act simply as a solvent, but by its solvent operation changes frequently the state of combination, and thus gives rise to new products. An example of this will be found at the end of this chapter, in the analysis of sea-water.

These various methods often require to be combined to obtain accurate results. From the mutual affinities of salts, and from their solubility in water depending so much on the proportions, nothing is more difficult than to produce their entire separation from a state of solution, particularly when small quantities of them are operated on, and when they are in complicated intermixtures. Repeated crystallizations, and the successive application of alkohol, are often necessary for this purpose; and in these repeated operations, much attention is necessary to guard against the loss of any of the ingredients.

By thus obtaining the solid ingredients separate, their quantities can be assigned either from their weight in a crystallized state, or in a state of desiccation at a certain fixed temperature. After exposure to a red heat, they are supposed to be free from water, or to be in what is called their *real* state; and it is best to refer to this as a standard; but with regard to some compounds, muriate of magnesia for example, or the carbonates, it is impracticable from the decomposition which they suffer. With regard to these, the best mode of estimating their weight in a real state, is to convert them into sulphates by the addition of sulphuric acid, and from the weight of the sulphate after exposure to a red heat, the *equivalent* weight of real muriate or carbonate may be found.

The quantities are also sometimes determined by estimation,—that is, they are inferred from discovering the quantities of the elements, and knowing the proportions in which these combine. Thus the quantity of sulphuric acid may be determined, by adding barytic water, or nitrate or muriate of barytes; it is precipitated in the state of sulphate of barytes; and the proportion of acid which a given weight of this brought to a certain state of desiccation contains, being known, the quantity may be inferred. The quantity of muriatic acid may be determined by the quantity of muriate of silver obtained by adding nitrate of silver to the mineral water; and the quantity of carbonic acid, by the quantity of carbonate formed by the addition of barytic or lime water. The quantities of certain of the bases may be discovered in a similar manner: that of lime may be discovered from the quantity of oxalate of lime precipitated by the addition of an oxalate, and that of magnesia or alumina by the direct precipitation of these earths by lime-water or ammonia. When the quantities of those bases which can be determined in this manner have been discovered, we discover whether these are in those proportions to the quantities of the acid obtained, which produce the state of neutralization, and therefore, whether other bases not producible in this method, as the fixed alkalis, are present: other methods are then had recourse to, from which the quantities of these are determined.

Some information, which may serve as a guide in the analysis of mineral waters, it has been supposed, may be derived from the knowledge of what are named Incompatible Salts, that is, salts which cannot exist together without producing decomposition and precipitation; as, if certain salts of this kind are discovered, it may be inferred, that others which are thus incompatible with them cannot be present. Thus, carbonate of soda and sulphate of lime, muriate of lime and sulphate of magnesia, muriate of lime and sulphate of soda, it might be concluded, could not exist together. But the accuracy of such conclusions is invalidated by the fact, that salts known to be incompatible, if their solutions were mixed in a concentrated state, are not so in a state of great dilution, owing to the solvent power of the water, increased by its quantity, on their principles, in consequence of which the power of cohesion, that determines to binary combinations, is counteracted, and these salts, with others considered incompatible, have accordingly been discovered together in mineral waters.

It had always been supposed, that the substances thus obtained from a mineral water are its real ingredients, and the perfection of the analysis was supposed to consist in their presence being recognized, and their quantities estimated with precision. There is every reason, however, to call this in question. The state of combination must frequently be liable to be modified by the analytic operations, and the substances obtained may be altogether different from those in solution.

This occurred to me more particularly, while submitting to analysis a newly discovered mineral water, that of Dunblane in Perthshire. It afforded by evaporation muriate of lime, muriate of soda, and sulphate of lime, an English pint yielding 18 grains of the first, 24 grains of the second, and 3.5 grains of the third. These, according to the common opinion, would have been considered as its ingredients. But it is quite possible to give a different view of its composition. The sulphuric acid may exist in it in the state of sulphate of soda; and when the solution is concentrated by evaporation, this salt re-acting on a portion of the muriate of lime, will form corresponding portions of muriate of soda, and sulphate of lime. On this view, a pint of the water will contain, estimating the equivalent quantities from the products of the evaporation, 20.8 of muriate of lime, 21 muriate of soda, and 3.7 sulphate of soda. And various considerations render this the more probable opinion.

It is obvious, that the substances obtained by evaporation from a compound saline solution, are not necessarily those which previously existed in it; for the concentration by the evaporation may, and in many cases must, change the actual combinations, and give rise to new products by decomposition. It is demonstrable, in the present case, that if muriate of lime and sulphate of soda existed in a state of dilute solution, they must be obtained by evaporation in the state of muriate of soda and sulphate of lime, since, whenever they were brought to a certain degree of concentration, they would re-act on each other, and form these combinations; and there is no possibility of proving, from the production of sulphate of lime with muriate of soda by evaporation, that either had existed as an original ingredient.

There are two views according to which the combinations in a compound saline solution,—that is, a solution containing more than one acid, and more than one base, might be supposed to be determined. The most obvious is, that they will be regulated by the respective forces of attraction, that those acids and bases will unite, and form binary compounds, which exert to each other the most powerful affinity; and as we have no accurate measure of the relative forces of affinity among bodies, it may be supposed that, on this principle, no certain conclusion can be drawn with regard to the state of combination.

The principle itself, however, is doubtful. Attraction is so much modified in its operation by external forces, that the combinations established are not always those arising from the most powerful attractions, but are frequently evidently dependent on the operation of these forces. This is apparent in the fact established by the most extensive induction, that in a compound saline liquid sufficiently concentrated to admit of the influence of the force of cohesion, those elements uniformly combine which form the least soluble compounds,—so much so indeed, that from a previous knowledge of their solubility, we can always predict with certainty what combinations will be established.

This leads, therefore, to another view. If the force of cohesion can so far modify chemical attraction, as to establish among compound salts dissolved in any medium, those combinations whence the least soluble compounds are formed, it may be inferred, that the reverse of this force, that is, the power of a solvent, may produce the opposite effect, or cause those combinations to be established, whence the compounds of greatest solubility are formed. If the elements constituting these are those which exert the most powerful attraction, this will concur with the effect of the solvent, and produce this result. If they are those which exert the weakest attractions, still the stronger attractions which would form the least soluble compound are counteracted by the power of the solvent, and the others are established. And hence will follow the general rule, that in any fluid containing the elements of compound salts, the binary compounds existing in it will be those which are most soluble in that fluid, and the reverse combinations will only be established by its concentration favouring the influence of the force of cohesion. In a solution containing sulphuric and muriatic acids, soda, and lime, the binary combinations must be those of sulphuric acid with soda, and muriatic acid with lime. And it is only from concentration of the solution that the reverse combinations will be established, of muriatic acid with soda, and sulphuric acid with lime.

Different facts are strictly conformable to this view: Thus, from many mineral waters, substances of sparing solubility, sulphate of lime for example, are obtained by evaporation, in much larger proportions than those in which they could exist in the water from their known solubility; they must therefore be regarded as products of the decomposition of more soluble compounds. Where such ingredients are deposited too, it generally happens, that the deposition commences after a certain extent of evaporation, then diminishes, and at length ceases, proving clearly, that the substance is not merely deposited as an original ingredient from the diminution in the quantity of solvent, for in this case its separation would continue to proceed to the end, but that it is formed at this stage of concentration by the re-action of compound salts, one or other of which is in limited quantity. In the evaporation of salt brines, for example, sulphate of lime falls down with muriate of soda after a certain degree of concentration, but the proportion of it becomes less as the evaporation proceeds: and in the evaporation of sea-water it is also deposited at first, but at length ceases to be produced, and the residual *bittern* is altogether free from it. Now it is obvious, that if in either case the sulphate of lime existed as an original ingredient, it would begin to be deposited when the evaporation had proceeded to that extent, that the remaining fluid was not sufficient to retain it dissolved, and that from that point it would continue to be deposited to the end: if, on the other hand, it does not pre-exist, but is formed from the action of sulphate of soda, or of magnesia, on muriate of lime, the result is precisely that to be expected; the mutual action must take place when a certain degree of concentration is attained, and when the muriate of lime is exhausted must cease. Lastly, the products obtained are often different, according to the nature of the analytic process employed, and the difference is conformable to the principle now illustrated. If sea-water, for example, be submitted to evaporation, it affords muriate of soda, muriate of magnesia, and sulphate of magnesia. If it be evaporated to dryness, and the dry mass be submitted to the action of alkohol, to separate the different salts, it affords muriate of soda, muriate of magnesia, and sulphate of soda. Since different products are thus obtained in these two methods, it is obvious, that the state of combination is modified in one or other of them, and the only explanation that can be given, is, that the evaporation from the aqueous solution, favours, by the influence of the force of cohesion, the production of muriate of soda and sulphate of magnesia, these being salts on the whole less soluble in water than the reverse combinations of muriate of magnesia and sulphate of soda: while the solvent power of alkohol with regard to muriate of magnesia has the opposite effect, favouring its production, and, of course, causing also that of sulphate of soda.

All these results, then, establish the general conclusion, that the ingredients obtained by evaporation from a mineral water, are not necessarily those which it held in solution, but are often products of the operation. Besides the example of sulphate of lime, which has been more particularly illustrated, as being probably always formed from the action of a soluble sulphate on muriate of lime, it may be inferred on the same grounds, that when carbonate of lime is obtained with muriate of soda, the original ingredients are carbonate of soda and muriate of lime; if carbonate of magnesia and muriate of soda are obtained, the ingredients previous to evaporation are probably carbonate of soda and muriate of magnesia: even sulphate of magnesia may be formed from the action of sulphate of soda on muriate of magnesia: and thus the real composition may be very different from the apparent composition inferred from the products of the analysis, more especially when the ingredients are numerous, and differ considerably in solubility. In general, it may be assumed, that substances of sparing solubility have not existed in previous solution, but are products of decomposition; and that the original combinations are those which form the most soluble compounds.

The mode in which the proportions are estimated according to this view, depends on the equivalent quantities of the different compound salts having been accurately ascertained. Thus, if sulphate of lime and muriate of soda be obtained by evaporation from a mineral water, we infer, that they have been formed from the mutual action of sulphate of soda and muriate of lime. We know what quantity of muriate of lime is equivalent to any given portion of sulphate of lime, 100 of the former being equivalent to 122.6 of the latter. We know also what quantity of muriate of soda must be formed along with a given quantity of sulphate of lime, from the re-action of sulphate of soda on muriate of lime, 107.7 being the quantity equivalent to 100 of muriate of lime, to 128 of sulphate of soda, and to 122.6 of sulphate of lime. Whatever quantity of sulphate of lime, then, is procured, that portion of it equivalent to the quantity of muriate of soda also obtained, is to be considered as formed by the action of sulphate of soda on muriate of lime; hence the quantities of the former give the equivalent quantities of the latter; and if there is any additional portion either of the sulphate of lime or of the muriate of soda above the equivalent, this must be considered either as an original ingredient, or as formed from the mutual decomposition of some other salts. In the same manner, from the quantities of carbonate of lime and muriate of soda, the quantities of carbonate of soda and muriate of lime may be inferred, and the method applies equally to all the other products of decomposition. The quantities in any particular case are at once obtained by inspection from Dr Wollaston's scale of chemical equivalents.

The subject now illustrated, is not merely one of speculation, but is of considerable practical importance in relation particularly to the medicinal virtues of mineral waters. The question has often been proposed, can these be accounted for from the results of chemical analysis? The conclusion would at once be drawn in the affirmative, when it is considered, that from the delicacy and accuracy of chemical researches, no active principle can be supposed to exist in a mineral water which analysis shall not be capable of discovering. Yet there are some difficulties on this subject, examples occurring in which the degree of activity is greater than could be inferred from the apparent composition, and in which even powers are exerted, where there appear no ingredients to the known operation of which they can be satisfactorily referred.

This probably arises from the composition in these cases having been inaccurately assigned. The existing combinations are changed by the analytic operations; soluble compounds are in particular converted into others which are insoluble, and which from this insolubility are comparatively inactive, and thus the real ingredients are disguised. The celebrated Bath Water is an example of this. The ingredients hitherto inferred from its analysis, as constituting its composition, are, in an English pint, about 9 grains of sulphate of lime, 3.3 grains of muriate of soda, 3 grains of sulphate of soda, $\frac{8}{10}$th of a grain of carbonate of lime, $\frac{1}{5}$ grain of silica, and $\frac{1}{70}$th grain of oxide of iron, —substances which are either altogether inert, or are in quantities so minute as, in the dose in which the water is taken, to be incapable of producing any sensible effect. But the real composition is probably very different; muriate of lime (a substance of considerable power) is the real ingredient; the quantity of it inferred from the above proportion of muriate of soda, is about 3.1 grains in a pint of the water, and on this, with a minute portion of muriate of iron, aided by the temperature, the active powers probably depend. Seltzer water, besides its large impregnation of carbonic acid, contains, according to Bergman's analysis, in a pint, 3 grains of carbonate of lime, 5 of carbonate of magnesia, 4 of carbonate of soda, and 17 of muriate of soda; it is one of the most active mineral waters in medicinal power, its medium dose being not more than half a pint, a degree of activity very inadequately accounted for by this composition. But on the principle now illustrated, the ingredients are, muriate of lime 3.3 grains, muriate of magnesia 5 grains, muriate of soda 7.8 grains, and carbonate of soda 10.3 real, or 18 crystallized,—a composition of much greater power, and conformable to the virtues assigned to it.

There is another point of view under which the state of combination in mineral waters may be considered. The acids and bases may be supposed to exist, not in those binary combinations which form the different compound salts, but in simultaneous combination, constituting properly one compound, the composition of which is subverted so as to form the binary compounds obtained, only by the influence of the force of cohesion exerted in the analytic operations. This no doubt may be maintained; for there is no conclusive proof of the actual existence of binary compounds previous to their being obtained by crystallization or precipitation; nor is there any direct improbability in the assumption, that in elements existing in a state of solution, having all of them mutual attractions, and exerting at the same time an attraction to the common solvent, an equilibrium may be produced, producing simultaneous combination, and mutual neutralization. On the other hand, it is equally possible, and perhaps more probable, that from the operation of different forces of attraction, and the influence of the solvent exerted more powerfully, in consequence of its relation to cohesion, to some substances than to others, binary combinations exist. And even admitting the opinion of simultaneous combination, this would afford a more satisfactory explanation of the powers of mineral waters, than the common opinion does, for the elements in such a combination may form an active compound, and one even possessed of specific qualities. It is only on the assumption, that the products obtained by evaporation are the ingredients, that the difficulty exists, the very process of evaporation causing the combinations to pass into that state in which the least active compounds are formed.

It is evident from the preceding observations, that the composition of Mineral Waters may be stated under very different points of view. It may be exhibited in conformity to the ingredients actually obtained by evaporation. It may be presented according to the principle, that those products which are of sparing solubility, are formed by decomposition, and that the binary compounds of greatest solubility are the original ingredients. Or it may be represented as consisting merely in the simultaneous combination of the different acids and bases, which the analysis indicates. It may be proper, in stating the results, to place them under all these points of view *.

The opinion which has now been illustrated, leads to

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* I refer for a more ample illustration of these views, to two Memoirs in the 7th volume of the Transactions of the Royal Society of Edinburgh,—One on the analysis of the Mineral Waters of Dunblane and Pitcaithly; the other on the analysis of Sea Water.

views of the analysis of Mineral Waters, different from those which have hitherto been adopted. It has always been supposed, that the composition is determined from the ingredients obtained by evaporation, or any analogous operation; this *direct* method of analysis, therefore, as it has been denominated, has been preferred, and the *indirect* method of inferring the results, by discovering the elements which constitute the binary compounds, and estimating their quantities, has only been occasionally employed as subordinate to the other, and to obviate particular difficulties. It must be apparent, however, that the one mode does not give the composition with more certainty than the other, for the salts obtained by evaporation are not necessarily the real ingredients, but are often products of decomposition, and therefore totally different. What the real ingredients are, must be inferred from some other principle, and when such a principle is established, a knowledge of the elements of the compounds,—that is, of the acids and bases present in the water, enables us to determine the composition with as much precision, as if the binary compounds were actually obtained. And this method has every advantage over the other, both in facility and accuracy. There is much difficulty in many cases in producing the perfect separation of salts from each other, and in reducing them to an uniform state of dryness, while nothing is more easy than discovering their elements, and estimating the quantities of these so as to determine the proportions of the compounds. On this principle, I have proposed a General Formula for the Analysis of Mineral Waters, which may be substituted, as applicable nearly in all cases, for the diversity of methods hitherto employed. An abstract of this, with the requisite details, I add from the original Memoir *.

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* Transactions of the Royal Society of Edinburgh, vol. viii.

The four classes of Carbonated, Sulphureous, Chalybeate, and Saline Waters, have been established. All of them, however, may be reduced in analysis under the last division. From those of the first class, the carbonic acid, which is in excess, is expelled by heat, and its quantity is estimated: from sulphureous waters, the sulphuretted hydrogen is in like manner disengaged; from the chalybeate waters, iron is obtained by its appropriate tests; and in all these cases the water remains with any saline impregnation, and of course is essentially the same with a water originally saline.

The salts usually contained in mineral waters are carbonates, sulphates, and muriates of lime, of magnesia, and of soda. Suppose a general knowledge of its ingredients to be gained by the use of re-agents and by evaporation; and suppose, for illustration, that all these are present, the following are the successive steps to be employed.

Reduce the water by evaporation as far as can be done without occasioning any sensible precipitation or crystallization; this, by the concentration, rendering the operation of the re-agents to be employed more certain.

Add to the liquor thus concentrated a saturated solution of muriate of barytes as long as any precipitation is produced, taking care to avoid adding an excess. If the precipitate effervesce with muriatic acid, and is entirely dissolved, it is carbonate of barytes, the weight of which gives the quantity of CARBONIC ACID; 100 grains, when dried, indicating 22 of carbonic acid. If it do not effervesce, it is sulphate of barytes, the weight of which, in like manner, gives the quantity of SULPHURIC ACID; 100 grains, dried at a low red heat, being equivalent to 34 of sulphuric acid. If it effervesce and is partially dissolved, it consists both of carbonate and sulphate, to ascertain the proportions of which let the precipitate be dried and weighed; then submitted to the action of dilute muriatic acid, and again washed, and dried at a low red heat; the weight of the residue will give the quantity of sulphate, and the loss of weight the quantity of carbonate of barytes.

The carbonic and sulphuric acids are thus removed and estimated, and the whole salts in the water are converted into muriates. It remains to discover and estimate their bases, and to find the quantity of muriatic acid originally contained.

Add to the clear liquor a saturated solution of oxalate of ammonia, as long as any precipitation takes place. The LIME is thus precipitated in the state of oxalate, which being calcined at a low red heat, is converted into carbonate, 100 of which are equivalent to 56 of lime; but as a little of the carbonic acid may be expelled, or a little water remain, it is better to convert it into sulphate by the addition of sulphuric acid; and this being exposed to a red heat, 100 grains of it are equivalent to 41.5 of lime.

The next step is to estimate the MAGNESIA. For this purpose, heat the clear liquor poured off after the precipitation of the oxalate of lime, to 100°, reducing it also, if it is dilute, by evaporation; add to it a solution of carbonate of ammonia, and immediately drop in a strong solution of phosphate of ammonia, continuing this addition with fresh portions, if necessary, of carbonate of ammonia, so as to preserve an excess of ammonia in the liquor, as long as any precipitation is produced. One portion of the ammonia neutralizes the acid of the magnesian salt, while another portion of it, uniting with the phosphoric acid and magnesia, forms the triple phosphate of magnesia and ammonia. The precipitate is washed; when exposed to a heat not exceeding 100°, it is dried without decomposition; and contains in this state, 0.19 of magnesia; but it is better, for the sake of accuracy, to convert it into phosphate of magnesia by calcination for an hour at a red heat: 100 grains then contain 40 of magnesia.

Evaporate the remaining liquor to dryness, and expose the dry matter to heat as long as any vapours exhale, raising it at the end to redness. The residue is muriate of soda, the weight of which gives the quantity of SODA, 100 grains being equivalent to 53.3.

The MURIATIC ACID in the muriate of soda obtained, may be either greater or less than that originally contained. To discover the real quantity, combine in binary compounds, according to their known proportions, the bases indicated in the analysis, with the acids, (taking the quantity of muriatic acid in the muriate of soda obtained). Any excess or deficiency of muriatic acid will then appear and the amount of the excess being subtracted from the quantity found in the muriate of soda, or the amount of the deficit being added to that quantity, the real quantity of muriatic acid will be determined. Or it may be directly inferred, from the addition of nitrate of silver or nitrate of lead to a given portion of the water from which the sulphuric and carbonic acids have been abstracted by nitrate of barytes, 100 grains of the precipitate of muriate of silver being equivalent to 19, and 100 grains of muriate of lead equivalent to 19.7 of muriatic acid.

Thus, by these methods, the different acids, and the different bases, are discovered, and their quantities determined. To complete the analysis, it remains to infer the state of combination in which they exist. The conclusions to be drawn with regard to this have been already illustrated. If binary compounds exist in a compound saline solution, the most probable conclusion is, that the compounds are those of greatest solubility. It may be proper, however, to state the results under all the points of view,—*first*, the quantities of the acids and bases, this affording what is certain, exclusive of all supposition; *secondly*, the quantities of the binary compounds inferred from the principle, that the most soluble compounds are the ingredients, which is not only the most probable view, but has the farther advantage of exhibiting the most active composition which can be assigned, and hence of best accounting for any medicinal powers; and, *thirdly*, the quantities of the binary compounds, such as they are obtained by evaporation, or any other direct analytic operation, which may sometimes be conformable to the real composition, and will always afford a possible view in contrast with the other.

The quantities of the acids and bases being found by the analysis, it is easy to assign the proportions of the compounds according to either view, by means of the scale of chemical equivalents.

Other substances which are of less common occurrence may be detected by particular methods. Silica will be decovered by the gelatinous consistence it gives on evaporation, and its remaining insoluble in acids, but soluble in alkalis. Alumina may be discovered by the water giving a precipitate with carbonate of ammonia, which is not soluble, or is only partially soluble in weak distilled vinegar, but is dissolved by boiling in a solution of potash; or by its precipitation, from the water sufficiently evaporated, by succinate of soda. Potash, when present, will remain at the end in the state of muriate of potash. Muriate of platina will detect its presence, and the muriate of potash may be separated by crystallization from the muriate of soda.

The following table presents the composition of some of the most celebrated mineral waters, according to the latest analyses, conformable to the common doctrine, that the substances obtained in the analysis are the real ingredients. With regard to many of them, there can be no doubt, but that the composition is modified by the analytic operations; and presented according to the view I have stated, it must in such cases exhibit very different results. As the accuracy, however, of many of the analyses on which the table is founded, cannot be regarded as certain, I have not thought it necessary to exhibit the composition according to this view, especially as it is easy in any particular case to infer the one from the other, in the manner which has been already explained.

Table of Mineral Waters.

WATERS.	Nitrogen.	Carbonic acid gas.	Sulphuretted hydrogen gas.	Carbonate of soda.	Carbonate of Magnesia.	Carbonate of Lime.	Sulphate of Soda.	Sulphate of Magnesia.	Sulphate of Lime.	Muriate of Soda.	Muriate of Magnesia.	Muriate of Lime.	Oxide of Iron.	Silica.	Temperature.
Carbonated.		cub. in.	cub. in.	grains.	grains.	grains.	grains.	grains.	grains.	grains.	grains.	grains.	grains.	grs.	
Seltzer,		138		32	40	24				140					Cold.
Pyrmont,		208			80	34.8		44.5	68.6	12.4			4.5		Cold.
Spa,		104		11.7	35.3	11.7				1.37			4.5		Cold.
Carlsbad,		32 to 50		39		12	70			34.6			0.125	2.5	165°
Sulphureous.															
Harrowgate,	7	8	19		5.5	18.5		10.5		615.5	91	13			Cold.
Moffat,	4	5	10							36					Cold.
Aix la Chap.			Supersulphuretted hydrogen.	90		38				40					143
Saline.															
Sedlitz,					21	6.7		1444	41.1		36.5				Cold.
Cheltenham,	12.	30.3	3		12.5		480		40	5	12.5		5		Cold.
Plombieres,				4.4		1	4.7			0.5				2.6	
Pitcaithly,		8				5			5.5	100		180			
Bristol,		30				13.5	11.2		11.7	4	7.25				74°
Buxton,	2					10.5			2.5	1.7			0.25		82°
Chalybeate.															
Tunbridge,	5	10.6							1.25	0.5	2.2		1		Cold.
Brighton,		18							32.7	12.2	6.		11.2	11.2	Cold.
Bath,		9.6				6.4	12		72	26.4			.016	1.6	116

Sea Water may be regarded as a Saline Mineral Water, containing only a much larger proportion than usual of saline matter. The proportion differs in different latitudes, according to the influence of evaporation. The water of the Atlantic in the warmer latitudes, contains about $\frac{1}{24}$ of saline matter; that of our shores, abstracting from the influence of fresh water, contains about $\frac{1}{30}$.

When sea water is submitted to evaporation, a large portion of muriate of soda crystallizes on the surface of the boiling liquor, small portions of carbonate and sulphate of lime are deposited; a concentrated liquor remains, Bittern, which, on farther evaporation, yields sulphate of magnesia, and muriate of magnesia remains in solution. Though these are the principal products, the precise composition has been variously stated by different chemists.

Bergman, from the analysis of sea water taken off the Canary Islands, and containing $\frac{1}{23}$ of saline matter, obtained as the products from a pint, reducing the proportion to that of our shores, or $\frac{1}{30}$, muriate of soda 186.5, muriate of magnesia 51, sulphate of lime 6 grains. Lavoisier gave as the composition of the water of the Atlantic from the coast of Normandy,—in a pound (French weight) 126 grains of muriate of soda, $14\frac{3}{4}$ muriate of magnesia, 23 muriate of lime mixed with muriate of magnesia, 7 sulphate of soda and sulphate of magnesia, and 8 of sulphate and carbonate of lime. More lately Vogel and Lagrange have given results more nearly approaching to those of Bergman, with the addition of sulphate of magnesia, the proportions from 1000 of sea water being 25.10 of muriate of soda, 3.5 muriate of magnesia, 5.78 sulphate of magnesia, 0.20 of carbonate of lime and magnesia, and 0.15 sulphate of lime. They state an analysis by Lichtenberg as similar to theirs: while in another by Pfaff, there is assigned a portion of muriate of lime.

Bergman's analysis is evidently incorrect in the omission of sulphate of magnesia. Lavoisier's is peculiar in assigning sulphate of soda, and still more muriate of lime, as ingredients, especially as these salts are incompatible in a strong solution, and might be supposed to be decomposed in the evaporation. Accordingly, in the experiments of Vogel and Lagrange, neither of them were obtained. The consideration of these uncertainties led me to undertake the analysis of sea water, and to conduct the results in reference to the principles already illustrated with regard to the state of combination in saline solutions, and the modifications produced by the usual analytic operations *.

By evaporation I found the products from a pint of sea water (taken from the Firth of Forth) to be muriate of soda 184 grains, muriate of magnesia 21.5, sulphate of magnesia 12.8, sulphate of soda 2, sulphate of lime 7.3=227.6.

Both Bergman and Lavoisier had employed alkohol in the analysis. Lavoisier's method consisted in evaporating to dryness; then submitting the dry mass to the action of successive portions of alkohol of different degrees of strength, to separate the salts. Following this method I found the results to be from a pint, muriate of soda 182.1 grains, muriate of magnesia 25.9, sulphate of soda 7.5, sulphate of magnesia 5.9, sulphate of lime 7.1.

It is evident from the diversity of results in these two methods, that the products depend in part on the analytic operations; nor could a better proof be adduced, that the substances obtained in such processes are not necessarily the real ingredients, for here they are different from the same solution, according to the method employed. The difference evidently arises from the operation of alkohol favouring the production of sulphate of soda; and this again may be ascribed to its action as a solvent. Muriate of soda and sulphate of magnesia are on the whole less so-

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* Transactions of the Royal Society of Edinburgh, vol. viii.

luble in water than sulphate of soda and muriate of magnesia; hence in evaporation the influence of cohesion determines their formation. But muriate of magnesia and sulphate of soda are on the whole more soluble in alkohol, especially when it is a little diluted, and therefore, in submitting the dry mass from evaporation to its solvent action, their production is favoured.

The composition of Sea Water may be represented under the different points under which, it has been already stated, that of saline mineral waters may be exhibited.

I. It may be supposed, that the different acids and bases are in simultaneous combination. Taking it in this light, I found by the process described in the preceding formula, that a pint contains sulphuric acid 14.4 grains, muriatic acid 97.7, soda 96.3, magnesia 14.8, lime 2.9=226.1.

II. Combining these according to the products of evaporation, the proportions will be muriate of soda 180.5 grains, muriate of magnesia 23, sulphate of magnesia 15.5, sulphate of lime 7.1.

III. Combining them according to the principle, that the compounds of greatest solubility are those which exist in solution, the proportions will be, muriate of soda 159.3 grains, muriate of magnesia 35.5, muriate of lime 5.7, sulphate of soda 25.6.

It can scarcely be doubted, but that the last view is just. The mode of analysis, too, by which these proportions were obtained, is the most accurate. And hence the last table may be considered as exhibiting the nighest approximation to the real composition of Sea Water.

The Water of the Dead Sea, in Palestine, it has been long known, has a strong impregnation of saline matter; its specific gravity is 1.211, and its taste is intensely bitter. From its analysis by Dr Marcet, it appears that 100 grains contain 3.92 of muriate of lime, 10.24 of muriate of magnesia, 10.36 of muriate of soda, and 0.054 of sulphate of lime.

END OF VOLUME THIRD.

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