PRINCIPLES OF CHEMISTRY

VOL. II.

THE

PRINCIPLES OF CHEMISTRY

By D. MENDELÉEFF

THIRD ENGLISH EDITION

TRANSLATED FROM THE RUSSIAN (SEVENTH EDITION) BY
GEORGE KAMENSKY, A.R.S.M.
OF THE IMPERIAL MINT, ST. PETERSBURG
AND
EDITED BY
THOMAS H. POPE, B.Sc., F.I.C.

IN TWO VOLUMES

VOLUME II.

LONGMANS, GREEN, AND CO.
39 PATERNOSTER ROW, LONDON
NEW YORK AND BOMBAY
1905

CONTENTS

OF

THE SECOND VOLUME

CHAPTER PAGE

XV. THE GROUPING OF THE ELEMENTS AND THE PERIODIC LAW 1

Isomorphism—Solid solutions—Isomorphous mixtures—The relation between the compositions of isomorphous bodies—Haüy's law—Homeomorphism—Hemimorphism, paramorphism—Morphotropy—The small number of simple forms of combination—The forms or compositions of the saline oxides—Suboxides—Peroxides—Limiting forms—The periodic dependence of the compositions or forms of combination of the elements on their atomic weights—Large and small periods—The zero group—Various modes of expressing periodic dependence—The correspondence between the elements and complex carbon radicles—The periodicity of the oxygen, hydrogen, and metallo-organic compounds of the elements—The positions of the elements in groups and series—The prediction of the properties of unknown elements—Its confirmation by the discovery of gallium and germanium—The employment of the periodic law to determine the atomic weights of the elements—The atomic weights do not merge into each other—The properties of the elements are functions of their mass—Chemical properties—The distribution of the elements in nature—The melting-point—Thermochemical properties—Alloys—Atomic volumes—Specific volumes—Apparent digressions from the periodic law—Tables expressing the periodic law.

XVI. ZINC, CADMIUM, AND MERCURY 48

Zinc sulphates, oxide of zinc—Chloride of zinc—Oxychloride of zinc—Metallic zinc—Action of acids on zinc—Zinc dust—Cadmium—Its salts—Mercury—Ores of mercury—Purification of mercury—Compounds of mercury—Oxides of mercury—Calomel—Corrosive sublimate—Basic salts of mercury—Diiodide and cyanide of mercury—Nitride of mercury—Amalgams—Eka-cadmium.

XVII. BORON, ALUMINIUM, AND THE ANALOGOUS METALS OF THE THIRD GROUP 70

Boron—Boric anhydride—Borax—The sublimation of boric anhydride with water—Boric acid and its salts—Boron in a free state—Nitride of boron—Fluoride of boron—Hydrofluoboric acid—Phosphide of boron—Chloride of boron—Aluminium—Clay—Kaolin—Levigation—Soils—Alumina—Hydrogel and

PRINCIPLES OF CHEMISTRY

CHAPTER XV

THE GROUPING OF THE ELEMENTS AND THE PERIODIC LAW

It is seen from the examples given in the preceding chapters that the analogies existing among the elements may be many-sided and more or less complete. Thus lithium and barium are in some respects analogous to sodium and potassium, and in others to magnesium and calcium. It is evident, therefore, that for a true judgment it is necessary to have, not only qualitative, but also quantitative and measurable data. When a property can be measured it ceases to be arbitrary, and renders the comparison objective.

Among these measurable properties of the elements and their corresponding compounds are: (*a*) isomorphism, or the analogy of crystalline forms; and, connected with it, the power to form crystalline mixtures which are isomorphous; (*b*) the relations between the volumes of analogous compounds of the elements; (*c*) the composition of their saline compounds; and (*d*) the relations of the atomic weights of the elements. In this chapter we shall briefly consider these four aspects of the matter, which are exceedingly important for a natural and fruitful grouping of the elements, facilitating, not only a general acquaintance with them, but also their detailed study.

Historically the first, and an important and convincing, method for finding a relationship between the compounds of two different elements is by means of **isomorphism.** This conception was introduced into chemistry by **Mitscherlich** (in 1820), who demonstrated that the corresponding salts of arsenic acid, H_3AsO_4, and phosphoric acid, H_3PO_4, crystallise with equal proportions of water, exhibit an exceedingly close resemblance in their crystalline form (as regards the angles of their faces and axes), and are able to crystallise together from solutions, forming crystals containing a mixture of these compounds. Isomorphous substances are those which, with the same number of atoms in their molecules, present analogous chemical reactions, a close resemblance in their properties, and a similar or very nearly similar crystalline form: they often contain certain elements in common, from which it is to be concluded that the remaining elements (as in the preceding example of As and P) are analogous to each other. And inasmuch as crystalline forms are capable of exact measurement, the external form is evidently as great a help in judging of the internal forces acting between the atoms as is a comparison of reactions, vapour densities, and other similar relations. We have already seen examples of this in the preceding pages.[1] It will be sufficient to call to mind that the compounds of the alkali metals with the halogens, RX, in a crystalline form, all belong to the cubic system and crystallise in octahedra or cubes—for example, sodium chloride, potassium iodide, rubidium chloride, &c. The nitrates of rubidium and cæsium appear in anhydrous crystals of the same form as potassium nitrate. The carbonates of the metals of the alkaline earths are isomorphous with calcium carbonate—that is, they appear either in forms like calc spar or in crystals of the rhombic system analogous to aragonite.[1a] Furthermore, sodium nitrate crystallises in rhombohedra, closely resembling the rhombohedra of calc spar (calcium carbonate), $CaCO_3$, whilst potassium nitrate appears in the same form as aragonite, $CaCO_3$, and the number of atoms in both kinds of salts is the same: they all contain one atom of a metal (K, Na, Ca), one atom of a non-metal (C, N), and three atoms of oxygen. The analogy of form evidently coincides with analogy of atomic composition. But the description of these salts shows that there is no close resemblance in their properties. It is evident that calcium carbonate approaches more nearly to magnesium carbonate than to sodium nitrate, although their crystalline forms are all very nearly the same. Isomorphous substances which are perfectly analogous to each other are characterised not only by a close resemblance of form (homeomorphism), but also by the faculty of entering into analogous reactions, which is not the case with RNO_3 and RCO_3. The most important and direct method of recognising perfect isomorphism—that is, the absolute analogy of two compounds—is given by that property of

---

[1] For instance the analogy of the sulphates of K, Rb, and Cs (Chap. XIII., note 1).

[1a] The crystalline forms of aragonite, strontianite, and witherite belong to the rhombic system; the angle of the prism is, for $CaCO_3$ 116° 10′, for $SrCO_3$ 117° 19′, and for $BaCO_3$ 118° 80′. On the other hand the crystalline forms of calc spar, magnesite, and calamine, which resemble each other quite as closely, belong to the rhombohedral system, with the angle of the rhombohedron for $CaCO_3$ 105° 8′, $MgCO_3$ 107° 10′, and $ZnCO_3$ 107° 40′. From this comparison it is at once evident that zinc is more closely allied to magnesium than magnesium to calcium.

analogous compounds of separating from solutions in homogeneous **crystals, containing the most varied proportions** of the analogous substances which enter into their composition. These quantities do not seem to be in dependence on the molecular or atomic weights, and if they are governed by any laws they must be analogous to those which apply to indefinite chemical compounds.[2] This will be clear from examples. Potassium chloride and potassium nitrate are not isomorphous with each other, and are in an atomic sense composed in a different manner. If these salts be mixed in a solution and the latter evaporated, independent crystals of the two salts will separate, each in that crystalline form which is proper to it. The crystals will not contain a mixture of the two salts. But if we mix the solutions of two isomorphous salts together, then, under certain circumstances, crystals will be obtained which contain both these substances. However, this cannot be taken as an absolute rule, for if we take a solution saturated at a high temperature with a mixture of potassium and sodium chlorides, on evaporation only sodium chloride will separate, and on cooling only potassium chloride. The first will contain very little potassium chloride, and the latter very little sodium chloride.[3] But if we take,

---

[2] Solutions furnish the commonest examples of indefinite chemical compounds. But the isomorphous mixtures which are so common among the crystalline compounds of silica forming the crust of the earth, as well as alloys, which are so important in the application of metals to the arts, are also instances of indefinite compounds. And if in Chap. I., and in many other portions of this work, it has been necessary to admit the presence of transitions to definite compounds (in a state of dissociation) in solutions, the same applies with even greater force to isomorphous mixtures and alloys. For this reason in many places in this work I refer to facts which compel us to recognise the existence of definite chemical compounds in all isomorphous mixtures and alloys. This view of mine (which dates from the sixties) upon isomorphous mixtures finds a particularly clear confirmation in the researches of B. Roozeboom (1892) (and in those of many others) upon the solubility and crystallising capacity of mixtures of the chlorates of potassium and thallium, $KClO_3$ and $TlClO_3$. He showed that when a solution contains different amounts of these salts, it deposits crystals containing either an excess of the first salt, from 98 per cent. to 100 per cent., or an excess of the second salt, from 63·7 to 100 per cent.; that is, in the crystalline form, either the first salt saturates the second, or the second the first, just as in the solution of ether in water; moreover, the solubilities of the mixtures containing respectively 36·3 and 98 per cent. of $KClO_3$ are the same, just as the vapour pressure of a saturated solution of water in ether is equal to that of a saturated solution of ether in water (Chap. I., note 47). But just as there are solutions miscible in all proportions, so also certain isomorphous bodies can be present in crystals in all possible proportions of their component parts. Van't Hoff calls such systems 'solid solutions.' These views were subsequently elaborated by Nernst (1892), and Witt (1891) applied them in explaining the phenomena observed in the coloration of tissues.

[3] The cause of the differences observed in different compounds of the same type, with respect to their property of forming isomorphous mixtures, must not be looked for in the difference of their volumetric composition, as has been affirmed by many investigators, including Kopp. The molecular volumes (found by dividing the molecular weight by the density) of those isomorphous substances which give intermixtures are not nearer to each other than the volumes of those which do not give such mixtures; for

for example, a mixture of solutions of magnesium sulphate and zinc sulphate, they cannot be separated from each other by evaporating the mixture, notwithstanding the rather considerable difference in solubility of these salts. Again, the isomorphous salts, magnesium carbonate and calcium carbonate, are found together—that is, in one crystal—in nature. The angle of the rhombohedron of these magnesia-lime spars is intermediate between the angles proper to the two separate spars (for calcium carbonate, the angle of the rhombohedron is 105° 8′; for magnesium carbonate, 107° 30′; and for $CaMg(CO_3)_2$, 106° 10′). Certain of these **isomorphous mixtures** of calc and magnesia spars appear in well-formed crystals, and in this case there not infrequently exists a simple molecular proportion of strictly definite chemical combination between the component salts—for instance, $CaCO_3,MgCO_3$—whilst in other cases, especially in the absence of distinct crystallisation (in dolomites), no such simple molecular proportion is observable: this is also the case in many artificially prepared isomorphous mixtures. The microscopical and crystallo-optical researches of Professor Inostrantzoff and others show that in many cases there is really a mechanical, although microscopically minute, juxtaposition in one whole of heterogeneous crystals of calcium carbonate (double refracting) and of the compound $CaMgC_2O_6$. If we suppose the adjacent parts to be microscopically small (on the basis of the researches of Mallard, Wyrouboff, and others), we obtain an idea of an isomorphous mixture. The composition of isomorphous mixtures is expressed by formulæ of general type; for instance, for spars, RCO_3, where $R = Mg$, Ca, and where it may be Fe, Mn, . . ., &c. This means that the Ca is partially replaced by Mg or another metal. Alums form a common example of the separation of isomorphous mixtures from solutions. They are double sulphates of alumina (or oxides isomorphous with it) and the alkalies, which crystallise in well-formed crystals. If aluminium sulphate is mixed with potassium sulphate, an alum separates, having the composition $KAlS_2O_8,12H_2O$. If sodium sulphate or ammonium

example, for magnesium carbonate the combining weight is 84, the density 3·06, and the volume therefore 27; for calcium carbonate in the form of calc spar the volume is 37, and in the form of aragonite 33; for strontium carbonate 41, for barium carbonate 46; that is, the volume of these closely allied isomorphous substances increases with the combining weight. The same is observed if we compare sodium chloride (molecular volume = 27) with potassium chloride (volume = 37), or sodium sulphate (volume = 55) with potassium sulphate (volume = 66), or sodium nitrate (39) with potassium nitrate (48), although the latter are less capable of giving isomorphous mixtures than the former It is evident that the cause of isomorphism cannot be explained by an approximation in the molecular volumes. It is more likely that, given a similarity in form and composition, the faculty to give isomorphous mixtures is connected with the degree of solubility and its variations. This view is supported by certain data belonging to the province of physical chemistry.

sulphate or rubidium (or thallium) sulphate be used, we obtain alums having the composition $RAlS_2O_8,12H_2O$. Not only do they all crystallise in the cubic system, but they also contain an equal molecular quantity of water of crystallisation ($12H_2O$). Besides which, if we mix solutions of the potassium and ammonium ($NH_4AlS_2O_8,12H_2O$) alums together, the crystals which separate will contain various proportions of the alkalies taken, and separate crystals of the alums of one or the other kind will not be obtained, but each separate crystal will contain both potassium and ammonium. Nor is this all; if we take a crystal of potassium alum and immerse it in a solution capable of yielding ammonia alum, the crystal of the potash alum will continue to grow and increase in size in this solution—that is, a layer of the ammonia or other alum will deposit itself upon the planes bounding the crystal of the potash alum. This is very distinctly seen if a colourless crystal of a common alum is immersed in a saturated violet solution of chrome alum, $KCrS_2O_8,12H_2O$, which then deposits itself in a violet layer over the colourless crystal of the alumina alum, as was observed even before Mitscherlich noticed it. If this crystal be then immersed in a solution of an alumina alum, a layer of this salt will form over the layer of chrome alum, so that one alum is able to incite the growth of the other. If the deposition proceed simultaneously, the resultant intermixture may be minute and inseparable, but its nature is understood from the preceding experiments; the attractive force of crystallisation of isomorphous substances is so nearly equal that the attractive power of an isomorphous substance induces a crystalline superstructure exactly the same as would be produced by the attractive force of like crystalline particles. From this it is evident that one isomorphous substance may **induce the crystallisation**[4] of another. Such a phenomenon explains, on the one hand, the aggregation of different isomorphous substances in one crystal, while, on the other hand, it serves as an indication of the nearness both of the molecular composition of isomorphous substances and of those forces which are proper to the elements distinguishing isomorphous substances. Thus, for example, ferrous sulphate or green vitriol crystallises in the monoclinic system, and contains seven molecules of water, $FeSO_4,7H_2O$, whilst copper vitriol crystallises with five molecules of water in the triclinic system, $CuSO_4,5H_2O$; nevertheless, it may be easily proved that both salts are perfectly isomorphous; that they are able to appear in identically the same forms and with equal molecular amounts of water. Marignac, by

---

[4] A phenomenon of a similar kind is shown for magnesium sulphate in note 27 of the last chapter. In the same example we see what complications the phenomena of dimorphism may introduce when the forms of analogous compounds are compared.

evaporating a mixture of sulphuric acid and ferrous sulphate under the receiver of an air-pump, first obtained crystals of the heptahydrated salt, and then of the pentahydrated salt $FeSO_4,5H_2O$, which were perfectly similar to the crystals of copper sulphate. Further, Lecoq de Boisbaudran, by immersing crystals of $FeSO_4,7H_2O$ in a supersaturated solution of copper sulphate, caused the latter to deposit in the same form as ferrous sulphate, in crystals of the monoclinic system, $CuSO_4,7H_2O$.

Hence it is evident that isomorphism—that is, the analogy of forms and the property of inducing crystallisation—may serve as a means for the discovery of analogies in molecular composition. We will take an example in order to render this clear. If, instead of aluminium sulphate, we add magnesium sulphate to potassium sulphate, then, on evaporating the solution, the double salt $K_2MgS_2O_8,6H_2O$ (Chap. XIV., note 28) separates instead of an alum, and the ratio of the component parts (in alums one atom of potassium per $2SO_4$, and here two atoms) and the amount of water of crystallisation (in alums 12, and here 6 equivalents per $2SO_4$) are quite different; nor is this double salt in any way isomorphous with the alums, nor capable of forming an isomorphous crystalline mixture with them, nor does the one salt provoke the crystallisation of the other. From this we must conclude that although alumina and magnesia, or aluminium and magnesium, resemble each other, they are not isomorphous, and that although they give partially similar double salts, these salts are not analogous to each other. And this is expressed in their chemical formulæ by the fact that the number of atoms in alumina or aluminium oxide, Al_2O_3, is different from the number in magnesia, MgO. Aluminium is trivalent and magnesium bivalent. Thus, having obtained a double salt from a given metal, it is possible to judge of the analogy of the given metal with aluminium or with magnesium, or of the absence of such an analogy, from the composition and form of this salt. Thus zinc, for example, does not form alums, but forms with potassium sulphate a double salt having a composition exactly like that of the corresponding salt of magnesium. It is often possible to distinguish the bivalent metals analogous to magnesium or calcium from the trivalent metals, like aluminium, by such a method. Furthermore, the specific heat and vapour density serve as guides. There are also indirect proofs. Thus iron gives ferrous compounds, FeX_2, which are isomorphous with the compounds of magnesium, and ferric compounds, FeX_3, which are isomorphous with the compounds of aluminium; in this instance the relative composition is directly determined by analysis, because, for a given amount of iron, $FeCl_2$ only contains two-thirds of the amount of chlorine which occurs in $FeCl_3$, and the composition of the corresponding oxygen compounds, i.e., of ferrous oxide, FeO, and ferric oxide, Fe_2O_3, clearly indicates the analogy of ferrous oxide with MgO and that of ferric oxide with Al_2O_3.

Thus in the building up of similar molecules in crystalline forms we see one of the numerous means for judging of the internal world of molecules and atoms. This method [5] has more than once been employed

---

[5] The property of solids of occurring in regular crystalline forms—the occurrence of many substances in the earth's crust in these forms—and those simple geometrical laws which govern the formation of crystals, long ago attracted the attention of the naturalist to crystals. The crystalline form is, without doubt, the expression of the relation in which the atoms occur in the molecules, and in which the molecules occur in the mass, of a substance. Crystallisation is determined by the distribution of the molecules along the direction of greatest cohesion, and therefore those forces must take part in the crystalline distribution of matter which act between the molecules; and, as they depend on the forces binding the atoms together in the molecules, a very close connection must exist between the atomic composition and the distribution of the atoms in the molecule on the one hand, and the crystalline form of a substance on the other; and hence an insight into the composition may be arrived at from the crystalline form. Such is the elementary and *a priori* idea which lies at the base of all researches into **the connection between composition and crystalline form.** Haüy, in 1811, established the following fundamental law, which has been worked out by later investigators: The fundamental crystalline form for a given chemical compound is constant (only the combinations vary), and with a change of composition the crystalline form also changes, naturally with the exception of such limiting forms as the cube, regular octahedron, &c., which may belong to various substances of the regular system. The fundamental form is determined by the angles of certain fundamental geometric forms (prisms, pyramids, rhombohedra), or the ratio of the crystalline axes, and is connected with the optical and many other properties of crystals. Since the establishment of this law the description of definite compounds in a solid state is accompanied by a description (measurement) of its crystals, which forms an invariable, definite, and measurable character. The most important epochs in the further history of this question were made by the following discoveries:—*Klaproth*, *Vauquelin*, and others showed that aragonite has the same composition as calc spar, whilst the former belongs to the rhombic and the latter to the hexagonal system. Haüy at first considered that the composition, and after that the arrangement, of the atoms in the molecules was different. This is dimorphism (see Chap. XIV., note 46). *Beudant*, *Frankenheim*, *Laurent*, and others found that the forms of the two nitres, KNO_3 and $NaNO_3$, exactly correspond with the forms of aragonite and calc spar; that they are able, moreover, to pass from one form into another; and that the difference of the forms is accompanied by a small alteration of the angles, for the angle of the prisms of potassium nitrate and aragonite is 119°, and that of sodium nitrate and calc spar, 120°; and therefore **dimorphism**, or the crystallisation of one substance in different forms, does not necessarily imply a great difference in the distribution of the molecules, although some difference clearly exists. The researches of *Mitscherlich* (1822) on the dimorphism of sulphur confirmed this conclusion, although it cannot yet be affirmed that in dimorphism the arrangement of the atoms remains unaltered, and that only the molecules are distributed differently. *Leblanc*, *Berthier*, *Wollaston*, and others already knew that many substances of different composition appear in the same forms, and crystallise together in one crystal. *Gay-Lussac* (1816) showed that crystals of potash alum continue to grow in a solution of ammonia alum. *Beudant* (1817) explained this phenomenon as the **assimilation** of a foreign substance by a substance having a great force of crystallisation, which he illustrated by many natural and artificial examples. But Mitscherlich, and afterwards *Berzelius* and *Heinrich Rose*

for discovering the analogy of elements and of their compounds; and as crystals are measurable, and their ability to form crystalline mix-

---

and others, showed that such an assimilation only exists with a similarity or approximate similarity of the forms of the individual substances and with a certain degree of chemical analogy. Thus was established the idea of **isomorphism** as an analogy of forms by reason of a resemblance of atomic composition, and by it was explained the variability of the composition of a number of minerals as isomorphous mixtures. Thus all the garnets are expressed by the general formula: $(RO)_3M_2O_3(SiO_2)_3$, where R = Ca, Mg, Fe, Mn, and M = Fe, Al, and where we may have either R and M separately, or their equivalent compounds, or their mixtures in all possible proportions.

But other facts, which render the correlation of form and composition still more complex, have accumulated side by side with a mass of data which may be accounted for by isomorphism and dimorphism. Foremost among the former stand the phenomena of **homeomorphism**—that is, a nearness of forms with a difference of composition—and then the cases of polymorphism and hemimorphism—that is, a nearness of the fundamental forms or only of certain angles for substances which are near or analogous in their composition. Instances of homeomorphism are very numerous. Many of these, however, may be reduced to a resemblance of atomic composition, although they do not correspond to an isomorphism of the component elements; for example, CdS (greenockite) and AgI, $CaCO_3$ (aragonite) and KNO_3, $CaCO_3$ (calc spar) and $NaNO_3$, $BaSO_4$ (heavy spar), $KMnO_4$ (potassium permanganate), and $KClO_4$ (potassium perchlorate), Al_2O_3 (corundum) and $FeTiO_3$ (titanic iron ore), FeS_2 (marcasite, rhombic system) and FeSAs (arsenical pyrites), NiS and NiAs, &c. But besides these instances, there are homeomorphous substances with an absolute dissimilarity of composition. Many such instances were pointed out by *Dana*. Cinnabar, HgS, and susannite, $PbSO_4,3PbCO_3$, appear in closely analogous crystalline forms; the acid potassium sulphate crystallises in the monoclinic system in crystals analogous to felspar, $KAlSi_3O_8$; glauberite, $Na_2Ca(SO_4)_2$, augite $RSiO_3$ (R = Ca,Mg), sodium carbonate, $Na_2CO_3,10H_2O$, Glauber's salt, $Na_2SO_4,10H_2O$ and borax, $Na_2BrO_7,10H_2O$, not only belong to the same system (monoclinic), but exhibit an analogy of combinations and approximately the same corresponding angles. These and many other similar cases might appear to be perfectly arbitrary (especially as a similarity of angles and fundamental forms is a relative idea) were there not other cases where a resemblance of properties and a distinct relation in the variation of composition is connected with a resemblance of form. Thus, for example, alumina, Al_2O_3 and water, H_2O, are frequently found in many pyroxenes and amphiboles which only contain silica and magnesia (MgO, CaO, FeO, MnO). *Scheerer* and *Hermann*, and many others, endeavoured to explain such instances by **polymetric isomorphism**, stating that MgO may be replaced by $3H_2O$ (for example, olivine and serpentine), SiO_2 by Al_2O_3 (in the amphiboles, talcs) and so on. A certain number of the instances of this order are subject to doubt, because many of the natural minerals which serve as the basis for the establishment of polymeric isomorphism, in all probability, no longer present their original composition, but one altered under the influence of solutions which have come into contact with them; they therefore belong to the class of **pseudomorphs**, or false crystals. There is, however, no doubt of the existence of a whole series of natural and artificial homeomorphs, which differ from each other by molecular proportions of water, silica, and some other component parts. Thus, *Thomsen* (1874) showed a very striking instance. The metallic chlorides, RCl_2, often crystallise with water, and they do not then contain less than one molecule of water per atom of chlorine. The most familiar representative of the order $RCl_2,2H_2O$ is $BaCl_2,2H_2O$, which crystallises in the rhombic system. Barium bromide, $BaBr_2,2H_2O$, and copper chloride, $CuCl_2,2H_2O$, have nearly the same forms. Potassium iodate, KIO_4; potassium chlorate, $KClO_4$; potassium permanganate, $KMnO_4$; barium sulphate, $BaSO_4$; calcium sulphate, $CaSO_4$; sodium sulphate, Na_2SO_4; barium formate, $BaC_2H_2O_4$, and others have almost the same crystalline form (of the rhombic system). Parallel with this series are those of the metallic chlorides of the form $RCl_2,4H_2O$, tures can be experimentally verified, this method is an objective one, and, as such, is in no sense arbitrary.

of the sulphates of the composition $RSO_4,2H_2O$, and of the formates $RC_2H_2O_4,2H_2O$. These compounds belong to the monoclinic system, have a close resemblance of form, and differ from the first series by containing two more molecules of water. The addition of two more molecules of water in all the above series also gives forms of the monoclinic system closely resembling each other; for example, $NiCl_2,6H_2O$ and $MnSO_4,4H_2O$. Hence we see that not only is $RCl_2,2H_2O$ analogous in form to RSO_4 and $RC_2H_2O_4$, but that their compounds with $2H_2O$ and with $4H_2O$ also exhibit closely analogous forms. From these examples it is evident that the conditions which determine a given form may be repeated not only in the presence of an isomorphous exchange—that is, with an equal number of atoms in the molecule—but also in the presence of an unequal number when there are peculiar and as yet ungeneralised relations in composition. Thus ZnO and Al_2O_3 exhibit a close analogy of form. Both oxides belong to the rhombohedral system, and the angle between the pyramid and the terminal plane is in the first 118° 7′, and in the second 118° 49′. Alumina, Al_2O_3, is also analogous in form to SiO_2, and we shall see that these analogies of form are conjoined with a certain analogy in properties. It is not surprising, therefore, that in the complex molecule of a silicious compound it is sometimes possible to replace SiO_2 by means of Al_2O_3, as Scheerer admits. The oxides Cu_2O, MgO, NiO, Fe_3O_4, CeO_2, crystallise in the regular system, although they are of very different atomic structure. *Marignac* demonstrated the perfect analogy of the forms of K_2ZrF_6 and $CaCO_3$, and the former is even dimorphous, like calcium carbonate. The same salt is isomorphous with R_2NbOF_5 and $R_2WO_2F_4$, where R is an alkali metal. There is an equivalency between $CaCO_3$ and K_2ZrF_6, because K_2 is equivalent to Ca, C to Zr, and F_6 to O_3, and with the isomorphism of the other two salts we find besides an equal content of the alkali metal—an equal number of atoms on the one hand and an analogy to the properties of K_2ZrF_6 on the other. The long-known isomorphism of the corresponding compounds of potassium and ammonium, KX and NH_4X, may be taken as the simplest example of the fact that an analogy of form shows itself with an analogy of chemical reaction even without an equality in atomic composition. Therefore the ultimate progress of the entire doctrine of the correlation of composition and crystalline forms will only be arrived at with the accumulation of a sufficient number of facts collected on a plan corresponding with the problems which here present themselves. The first steps have already been made. The researches of the Geneva savant, *Marignac*, on the crystalline form and composition of many of the double fluorides, and the work of *Wyrouboff* on the ferricyanides and other compounds, are particularly important in this respect.

It is already evident that, with a definite change of composition, certain angles remain constant, notwithstanding that others are subject to alteration. Such an instance of the relation of forms was observed by *Laurent*, and named by him **hemimorphism** (an anomalous term) when the analogy is limited to certain angles, and **paramorphism** when the forms in general approach each other, but belong to different systems. Thus, for example, the angle of the planes of a rhombohedron may be greater or less than 90°, and therefore such acute and obtuse rhombohedra may closely approximate to the cube. Hausmannite, Mn_3O_4, belongs to the tetragonal system, and the planes of its pyramid are inclined at an angle of about 118°, whilst magnetic iron ore, Fe_3O_4, which resembles hausmannite in many respects, appears in regular octahedra—that is, the pyramidal planes are inclined at an angle of 109° 28′. This is an example of paramorphism; the systems are different, the compositions are analogous, and there is a certain resemblance in form. Hemimorphism has been found in many instances of saline and other substitutions. Thus, *Laurent* demonstrated, and *Hintze* confirmed (1873), that naphthalene derivatives of analogous composition are hemimorphous. *Nicklès* (1849) showed that in ethylene sulphate the angle of the prism is 125° 26′, and in the nitrate of the same radicle 126° 35′. The angle of the prism of methylamine oxalate is 131° 20′, and with the fluoride, which is very different in composition from the former, the angle is 132°

The regularity and simplicity expressed by the exact laws of crystalline form repeat themselves in the aggregation of the atoms to form molecules. Here, as there, there are but few forms which are essentially different, and their apparent diversity reduces itself to a few fundamental differences of type. There the molecules aggregate themselves into crystalline forms; here, the atoms aggregate themselves into molecular forms or into **the types of compounds.** In both cases the fundamental crystalline or molecular forms are liable to variations, conjunctions, and combinations. If we know that potassium gives compounds of the fundamental type KX, where X is a univalent element (which combines with one atom of hydrogen, and is, according to the law of substitution, able to replace it), then we know the composition of its compounds: K_2O, KHO, KCl, NH_2K, KNO_3, K_2SO_4, $KHSO_4$, $K_2Mg(SO_4)_2,6H_2O$, &c. All the possible derivative crystalline forms are not known. So also all the atomic combinations are not known for every element. Thus in the case of potassium, KCH_3, K_3P, K_2Pt, and other like compounds which exist for hydrogen or chlorine are unknown.

The majority of the fundamental types for the building up of atoms into molecules are already known to us. If X stand for a univalent element, and R for an element combined with it, then eight atomic types may be observed:—

$$RX,\ RX_2,\ RX_3,\ RX_4,\ RX_5,\ RX_6,\ RX_7,\ RX_8.$$

Groth (1870) endeavoured to indicate in general what kinds of change of form proceed with the substitution of hydrogen by various other elements and groups, and he observed a regularity which he termed **morphotropy**. The following examples show that morphotropy recalls the hemimorphism of Laurent. Benzene, C_6H_6, rhombic system, ratio of the axes 0·891 : 1 : 0·799. Phenol, $C_6H_5(OH)$, and resorcinol, $C_6H_4(OH)_2$, also rhombic system, but one axial ratio is changed, the numbers for resorcinol being 0·910 : 1 : 0·540—that is, a portion of the crystalline structure in one direction is the same, but in the other direction it is changed, whilst in the rhombic system dinitrophenol, $C_6H_3(NO_2)_2(OH)$ = 0·833 : 1 : 0·753; trinitrophenol (picric acid), $C_6H_2(NO)_3(OH)$ = 0·937 : 1 : 0·974; and the potassium salt = 0·942 : 1 : 1·354. Here the ratio of the first pair of axes is preserved—that is, certain angles remain constant, and the chemical proximity of the composition of these bodies is undoubted. Laurent compares hemimorphism with architectural style. Thus, Gothic cathedrals differ in many respects, but there is an analogy expressed both in the sum total of their common relations and in certain details—for example, in the windows. It is evident that we may expect many fruitful results for molecular mechanics (which forms a problem common to many provinces of natural science) from the further elaboration of the data concerning those variations which take place in crystalline form when the composition of a substance is subjected to a known change, and I therefore consider it useful to point out to the student of science seeking for matter for independent scientific research this vast field for work which is presented by the correlation of form and composition. The geometrical regularity and varied beauty of crystalline forms offer no small attraction to research of this kind.

Let X be chlorine or hydrogen. Then examples of the first type will be: H_2, Cl_2, HCl, KCl, NaCl, &c. The compounds of oxygen or calcium may serve as examples of the type RX_2: OH_2, OCl_2, OHCl, CaO, $Ca(OH)_2$, $CaCl_2$, &c. For the third type RX_3 we know the representative NH_3 and the corresponding compounds N_2O_3, NO(OH), NO(OK), PCl_3, P_2O_3, PH_3, SbH_3, Sb_2O_3, B_2O_3, BCl_3, Al_2O_3, &c. The type RX_4 is known among the hydrogen compounds. Marsh gas, CH_4, and its corresponding saturated hydrocarbons, C_nH_{2n+2}, are the best representatives. Also CH_3Cl, CCl_4, $SiCl_4$, $SnCl_4$, SnO_2, CO_2, SiO_2, and a whole series of other compounds come under this class. The type RX_5 is also already familiar to us, but there are no purely hydrogen compounds among its representatives. Sal-ammoniac, NH_4Cl, and the corresponding $NH_4(OH)$, $NO_2(OH)$, $ClO_2(OK)$, as well as PCl_5, $POCl_3$, &c., are representatives of this type. In the higher types also there are no hydrogen compounds, but in the type RX_6 there is the chlorine compound WCl_6, and a fluorine one, SF_6. However, there are many oxygen compounds, and among them SO_3 is the best known representative. To this class also belong $SO_2(OH)_2$, SO_2Cl_2, $SO_2(OH)Cl$, CrO_3, &c., all of an acid character. Of the higher types there are in general only oxygen and acid representatives. The type RX_7 we know in perchloric acid, $ClO_3(OH)$, and potassium permanganate, $MnO_3(OK)$, is also a member. The type RX_8 in a free state is very rare; osmic anhydride, OsO_4, is the best known representative of it.[6]

---

[6] The still more complex combinations—which are so clearly expressed in the crystallo-hydrates, double salts, and similar compounds—although they may be regarded as independent, are, however, most easily understood with our present knowledge as aggregations of whole molecules to which there are no corresponding double compounds, containing one atom of an element R and many atoms of other elements RX_n The above types embrace all cases of direct combinations of atoms, and the formula $MgSO_4,7H_2O$ cannot, without violating known facts, be directly deduced from the types MgX_n or SX_n, whilst the formula $MgSO_4$ corresponds both with the type of the magnesium compounds MgX_2 and with the type of the sulphur compounds SO_2X_2, or in general SX_6, where X_2 is replaced by $(OH)_2$, with the substitution in this case of H_2 by the atom Mg, which always replaces H_2. However, it must be remarked that the sodium crystallo-hydrates often contain $10H_2O$, the magnesium crystallo-hydrates 6 and $7H_2O$, and that the type PtM_2X_6 is proper to the double salts of platinum, &c. With the further development of our knowledge concerning crystallo-hydrates, double salts, alloys, solutions, &c., *in the chemical sense* of feeble compounds (that is, such as are easily destroyed by feeble chemical influences) it will probably become possible to arrive at a perfect generalisation for them. For a long time these subjects were only studied by the way or by chance; our knowledge of them is accidental and destitute of system, and it is therefore impossible to expect as yet any generalisation as to their nature. It is not long since the days of Gerhardt when only three types were recognised: RX, RX_2, and RX_3; the type RX_4 was afterwards added (by Cooper, Kekulé, Butleroff, and others), mainly for the purpose of generalising the data respecting the carbon compounds. And indeed many are still satisfied with these types, and derive the higher types from them; for instance, RX_5 from RX_3—as, for example, $POCl_3$, from PCl_3, considering the oxygen

The four lower types RX, RX_2, RX_3, and RX_4 are met with in compounds of the elements R with chlorine and oxygen, and also in their compounds with hydrogen, whilst the four higher types only appear for such acid compounds as are formed by chlorine, oxygen, and similar elements. Among the oxygen compounds the **saline oxides** which are capable of forming salts either through the function of a base or through the function of an acid oxide attract the greatest interest in every respect. Certain elements, like calcium and magnesium, only give one saline oxide—for example, MgO, corresponding with the type MgX_2. But the majority of the elements appear in several such forms. Thus copper gives CuX and CuX_2, or Cu_2O and CuO. If an element R gives a higher type RX_n, then there often also exist, as if by symmetry, lower types, RX_{n-2}, RX_{n-4}, and in general such types as differ from RX_n by an even number of X. Thus in the case of sulphur the types SX_2, SX_4, and SX_6 are known—for example, SH_2, SO_2, and SO_3. The last type is the highest, SX_6. The types SX_5 and SX_3 do not exist. But even and uneven types sometimes appear for one and the same element. Thus the types RX and RX_2 are known for copper and mercury.

Among the **saline** oxides only the **eight types** enumerated below are known to exist. They determine the possible formulæ of the compounds of the elements, if it be taken into consideration that an element which gives a certain type of combination may also give lower types. For this reason the rare type of the **suboxides** or *quaternary* oxides R_4O (for instance, AG_4O, AG_2Cl) is not characteristic; it is always accompanied by one of the higher grades of oxidation, and the compounds of this type are distinguished by their great chemical instability, and split up into an element and the higher compound (for instance, $Ag_4O = 2Ag + Ag_2O$). Many elements, moreover, form transition oxides, which have an intermediate composition and are able, like N_2O_4, to split up into the lower and higher oxides. Thus iron gives magnetic oxide, Fe_3O_4, which is in all respects (by its reactions) a compound of the suboxide FeO with the oxide Fe_2O_3.

to be bound both to the chlorine (as in HClO) and to the phosphorus. But the time has now arrived when it is clearly seen that the forms RX, RX_2, RX_3, and RX_4 do not exhaust the whole variety of phenomena. The revolution became evident when Würtz showed that PCl_5 is not a compound of $PCl_3 + Cl_2$ (although it may decompose into two molecules), but a whole molecule capable of passing into vapour as PCl_5 like PF_5 and SiF_4. The time for the recognition of types even higher than RX_8 is in my opinion in the future; that it will come we can already see in the fact that oxalic acid, $C_2H_2O_4$, gives a crystallo-hydrate with $2H_2O$, which may be referred to the type CH_4, or rather to the type of ethane, C_2H_6, all the atoms of hydrogen of which are replaced by hydroxyl, $C_2H_2O_4,2H_2O = C_2(OH)_6$ (see Chap. XXII., note 35).

The independent and more or less stable saline compounds correspond with the following eight types :—

R_2O ; salts RX, hydroxides ROH. Generally basic like K_2O, Na_2O, Hg_2O, Ag_2O, Cu_2O ; though there are acid oxides of this composition, they are very rare, are only formed by distinctly acid elements, and even then have only feeble acid properties ; for example, Cl_2O and N_2O.

R_2O_2 or RO ; salts RX_2, hydroxides $R(OH)_2$. The most simple basic salts R_2OX_2 or $R(OH)X$; for instance, the chloride Zn_2OCl_2 ; also an almost exclusively basic type ; but the basic properties of the oxides of this type are more feebly developed than in the preceding type. For example, CaO, MgO, BaO, PbO, FeO, MnO, &c.

R_2O_3 ; salts RX_3, hydroxides $R(OH)_3$, $RO(OH)$, the most simple basic salts ROX, $R(OH)X_3$. The bases are feeble, like Al_2O_3, Fe_2O_3, Tl_2O_3, Sb_2O_3. The acid properties are also feebly developed ; for instance, in B_2O_3 ; but with the non-metals the properties of acids are already clear ; for instance, P_2O_3, $P(OH)_3$.

R_2O_4 or RO_2 ; salts RX_4 or ROX_2, hydroxides $R(OH)_4$, $RO(OH)_2$. Rarely bases (feeble), like ZrO_2, PtO_2 ; more often acid oxides ; but the acid properties are in general feeble, as in CO_2, SO_2, SnO_2. Many intermediate oxides appear in this and the preceding and following types.

R_2O_5 ; salts principally of the types ROX_3, RO_2X, $RO(OH)_3$, $RO_2(OH)$, rarely RX_5. The basic character is feeble ; the acid character predominates, as is seen in N_2O_5, P_2O_5, Cl_2O_5, and then $X = OH$, OK, &c. ; for example, $NO_2(OK)$.

R_2O_6 or RO_3 ; salts and hydroxides generally of the type RO_2X_2, $RO_2(OH)_2$. Oxides of an acid character, as SO_3, CrO_3, MnO_3. Basic properties rare and feebly developed as in UO_3.

R_2O_7 ; salts of the form RO_3X, $RO_3(OH)$, acid oxides ; for instance, Cl_2O_7, Mn_2O_7. Basic properties as feebly developed as the acid properties in the oxides R_2O.

R_2O_8 or RO_4. A very rare type, and only known in OsO_4 and RuO_4.

The majority of the ordinary elements appear in the first seven types, and if a given element gives oxides of one of the higher types, it is also able to form all the lower oxides ; for example, nitrogen.

It is evident from the circumstance that in all the higher types **the acid hydroxides** (for example, $HClO_4$, H_2SO_4, H_3PO_4) and salts with a single atom of one element **contain**, like the higher saline type RO_4, **not more than four atoms of oxygen** ; that the formation of the saline oxides is governed by a certain common principle which is best looked for in the fundamental properties of oxygen, and in general of the most simple compounds. The hydrate of the oxide RO_2 is of the higher type $RO_2,2H_2O = RH_4O_4 = R(HO)_4$. Such, for example, is the hydrate of silica and the salts (orthosilicates) corresponding with it, $Si(MO)_4$. The oxide R_2O_5 corresponds with the hydrate $R_2O_5,3H_2O = 2RH_3O_4 = 2RO(OH)_3$. Such is orthophosphoric acid, PH_3O_4. The hydrate of the oxide RO_3 is $RO_3,H_2O = RH_2O_4 = RO_2,(OH)_2$—for instance, sulphuric acid. The hydrate corresponding to R_2O_7 is evidently $RHO_4 = RO_3(OH)$—for example, perchloric acid. Here, besides containing O_4, it must further be remarked that **the amount of hydrogen in the hydrate is equal to the amount of hydrogen in the hydrogen compound.** Thus silicon gives SiH_4 and SiH_4O_4, phosphorus PH_3 and PH_3O_4, sulphur SH_2 and SH_2O_4, chlorine ClH and $ClHO_4$. This connects in a harmonious and general system the fact that **the elements are capable of combining with a greater amount of oxygen, the less the amount of hydrogen which they are able to retain.** In this the key to the comprehension of all further deductions must be looked for, and we shall therefore formulate this rule in general terms. An element R gives a hydrogen compound RH_n, the hydrate of its higher oxide will be RH_nO_4, and therefore the higher oxide will contain $2RH_nO_4 - nH_2O = R_2O_{8-n}$. For example, chlorine gives $ClH(n=1)$, the hydrate $ClHO_4$, and the higher oxide Cl_2O_7. Carbon gives CH_4 and CO_2. So, also, SiO_2 and SiH_4 are the higher compounds of silicon with hydrogen and oxygen, like CO_2 and CH_4. Here the amounts of oxygen and hydrogen are equivalent. Nitrogen combines with a large amount of oxygen, forming N_2O_5, but, on the other hand, with a small quantity of hydrogen in NH_3. *The sum of the equivalents of hydrogen and oxygen*, occurring in combination with an atom of nitrogen, is, as always in the higher types, equal to *eight*. It is the same with the other elements which combine with hydrogen and oxygen. Thus sulphur gives SO_3; consequently, six equivalents of oxygen fall to an atom of sulphur, and in SH_2 two equivalents of hydrogen. The sum is again equal to eight. The relation between Cl_2O_7 and ClH is the same. This shows that the property of elements of combining with such different elements as oxygen and hydrogen is subject to one common law, which is also formulated in the system of the elements presently to be described.[7] Just as for hydrogen, besides water H_2O, which forms an example of

---

[7] Not wishing to complicate the explanation, I only touch here on the general features of the relation between the hydrates and oxides and of the oxides among themselves. Thus, for instance, the conception of the ortho-acids and of the normal acids will be considered in speaking of phosphoric and phosphorous acids.

the saline oxides and the only saline compound of hydrogen, there also exists the peroxide of hydrogen H_2O_2, with a series of peculiar reactions which distinguish it from the saline oxides, so also the majority of other elements have, often, if not always, besides their corresponding saline oxides, their **peroxides**, containing more oxygen than the higher saline oxides and capable not only of entering into peculiar reactions like those of peroxide of hydrogen, but also of forming peroxide of hydrogen under many circumstances, and often of being formed either from H_2O_2, or under the same conditions as H_2O_2.[7a] A slight acquaintance with bases, acids and salts, and with peroxide of hydrogen, removes all doubt as to whether a given oxide or its hydrate should be referred to the class of saline oxides or of peroxides, even if there be salts corresponding to the peroxide. Persulphuric acid, $H_2S_2O_8$, which possesses the well-marked properties of a peroxide, as will be seen in describing it (Chap. XX.), is an instance in question. What was said above about oxides, and what will be further said respecting them, refers exclusively to the saline oxides, all the more so as the peroxides (and among them persulphuric acid) have been studied far less than the saline oxides and the same grouping and degree of analogy among the elements is seen in their faculty to form peroxides as in the case of true saline oxides.[7b]

In the preceding relation between the faculty of the elements to combine with oxygen and hydrogen we see not only the regularity and simplicity which govern the formation and properties of the saline oxides and of all the compounds of the elements, but also a fresh and exact means for recognising the analogy between elements. Analogous elements give compounds of analogous types, both higher and lower. If CO_2 and SO_2 are two gases which closely resemble each other both in their physical and chemical properties, the reason of this must be looked for not in an analogy of sulphur and carbon, but in that identity of the type of combination, RX_4, which both oxides assume, and in that influence which a large mass of oxygen always exerts on the

---

[7a] In many such cases taking place in the presence of water, and where the water is retained, it is difficult to say whether the oxygen is held in the peroxide of the element or in the form of peroxide of hydrogen. Thus molybdenum, for instance, gives a higher oxide, MoO_3, and it also forms a hydrate of the peroxide, $Mo_2H_2O_8 = Mo_2O_7,H_2O$. This may, however, be regarded as a compound of oxide of molybdenum with peroxide of hydrogen, $Mo_2H_2O_8 = 2MoO_3 + H_2O_2$, just as compounds of peroxide of hydrogen with BaO_2, &c., are known (Chap. IV.).

[7b] There is no doubt that analogous elements very often give analogous peroxides, and a study of the peroxides supports the periodic system of the elements, as the researches of Piccini, Melikoff, Pissarjewsky, and others show. The subject is, however, as yet poor in facts, and the peroxides evince but few direct relations to the radical properties of the elements, and therefore I think that a general systematisation of the peroxides is a matter of the future.

properties of its compounds. In fact, there is little resemblance between carbon and sulphur, as is seen not only from the fact that CO_2 is the *higher form* of oxidation, whilst SO_2 is able to further oxidise into the higher oxide SO_3, but also from the fact that all the other compounds—for example, SH_2 and CH_4, SCl_2 and CCl_4, &c.—are entirely unlike both in type and in chemical properties. This absence of analogy in carbon and sulphur is especially clearly seen in the fact that the highest saline oxides are of different composition, CO_2 for carbon, and SO_3 for sulphur. In Chapter VIII. we considered the limit to which carbon tends in its compounds, and in a similar manner there is for every element a tendency to attain a certain highest limit RX_n in its compounds. This view was particularly developed in the middle of the nineteenth century by Frankland in studying the organo-metallic compounds, i.e., those in which X is wholly or partially a hydrocarbon radicle; for instance, $X=CH_3$ or C_2H_5 &c. Thus, for example, antimony, Sb (Chap. XIX.) gives, with chlorine, compounds $SbCl_3$ and $SbCl_5$ and corresponding oxygen compounds Sb_2O_3 and Sb_2O_5, whilst under the action of CH_3I, C_2H_5I, or in general EI (where E is a hydrocarbon radicle of the paraffin series), upon antimony or its alloy with sodium there are formed SbE_3 (for example, $Sb(CH_3)_3$, boiling at about 81°), which, corresponding to the lower form of combination SbX_3, are able to combine further with EI, or Cl_2, or O, and to form compounds of the limiting type SbX_5; for example, SbE_4Cl, corresponding to NH_4Cl with the substitution of nitrogen by antimony, and of hydrogen by the hydrocarbon radicle. The elements, which are most chemically analogous, are characterised by the fact of their giving compounds of similar form RX_n. The halogens, which are analogous, give both higher and lower compounds.[7c] So also do the metals of the alkalies and of the alkaline earths. And we saw that this analogy extends to the composition and properties of the carbon, nitrogen, and hydrogen compounds of these metals, as is best seen in the salts. Many such groups of analogous elements have long been known. Thus there are analogues of oxygen, nitrogen, and carbon, and we shall meet with many such groups. But an acquaintance with them inevitably leads to the questions, What is the cause of the analogy and what is the relation of one group to another? If these questions remain

---

[7c] The analogy of the types of combination of the halogens is partly destroyed by fluorine, which gives higher types with greater ease than Cl; thus it forms SF_6 (Chap. XX.) with sulphur, and IF_5 with iodine, which chlorine does not. **Pentafluoride of iodine** was obtained by Moissan (1902) by the direct action of fluorine on iodine. It is a colourless liquid which solidifies at +8°, boils at 97° without decomposition, and decomposes at about 500°. It is highly hygroscopic, and in general presents many remarkable reactions.

unanswered, it is easy to fall into error in the formation of the groups, because the notions of the degree of analogy will always be relative, and will not present any accuracy or distinctness. Thus lithium is analogous in some respects to potassium and in others to magnesium; beryllium is analogous to both aluminium and magnesium. Thallium, as we shall afterwards see and as was observed on its discovery, has much kinship with lead and mercury, but in some of its properties it resembles lithium and potassium. Naturally, where it is impossible to make measurements one is reluctantly obliged to limit oneself to approximate comparisons, founded on arbitrarily chosen data which are often wanting in exactitude. But in the elements there is one accurately measurable property, which is subject to no doubt—namely, that property which is expressed in their atomic weights. Its magnitude indicates the relative mass of the atom, or, if we avoid the conception of the atom, its magnitude shows the relation between the masses forming the chemical and independent individuals or elements. And according to the teaching of all exact data concerning the phenomena of nature, *the mass of a substance is that property on which all its remaining properties must be dependent*, because they are all determined by similar conditions or by those forces which act in determining the weight of a substance, and this is directly proportional to its mass. Therefore it is most natural to seek for a dependence between the properties and analogies of the elements on the one hand and their atomic weights on the other.

This is the fundamental idea which leads **to arranging all the elements according to their atomic weights.** A periodic repetition of properties is then immediately observed in the elements. We are already familiar with examples of this :—

F = 19, Cl = 35·5, Br = 80, I = 127,
Na = 23, K = 39, Rb = 85, Cs = 133,
Mg = 24, Ca = 40, Sr = 87, Ba = 137.

The essence of the matter is seen in these groups. The halogens have smaller atomic weights than the alkali metals, and the latter than the metals of the alkaline earths. A logical development and generalisation of this fact leads us to conclude that, **if all the elements are arranged in the order of their atomic weights, a periodic repetition of properties is obtained.** This is expressed by the **law of periodicity**; *the properties of the elements, as well as the forms and properties of their compounds, are in periodic dependence on, or (expressing ourselves algebraically) form a periodic function of, the atomic weights of* *the elements.*[8] The table of the **periodic system of the elements**, with the values of the atomic weights proper to them in ascending order,

---

[8] The periodic law and the periodic system of the elements appeared in the same form as here given in the first edition of this work, begun in 1868 and finished in 1871. In laying out the accumulated information respecting the elements, I had occasion to reflect on their mutual relations. At the beginning of 1869 I distributed among many chemists a pamphlet entitled *An Attempted System of the Elements, based on their Atomic Weights and Chemical Analogies*, and at the March meeting of the Russian Chemical Society, 1869, I communicated a paper *On the Correlation of the Properties and Atomic Weights of the Elements.* The substance of this paper is embraced in the following conclusions: (1) the elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties. (2) Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (platinum, iridium, osmium) or which increase regularly (e.g., potassium, rubidium, cæsium). (3) The arrangement of the elements or of groups of elements in the order of their atomic weights corresponds with their so-called *valencies.* (4) The elements which are the most widely distributed in nature have *small* atomic weights, and all the elements of small atomic weight are characterised by sharply defined properties. They are therefore typical elements. (5) The *magnitude* of the atomic weight determines the character of an element. (6) The discovery of many yet unknown elements may be expected. For instance, elements analogous to aluminium and silicon, whose atomic weights would be between 65 and 75. (7) The atomic weight of an element may sometimes be corrected by the aid of a knowledge of those of the adjacent elements. Thus the combining weight of tellurium must lie between 123 and 126, and cannot be 128. (8) Certain characteristic properties of the elements can be foretold from their atomic weights.

The entire periodic law is included in these lines. In the series of subsequent papers (1870–72, for example, in the *Transactions* of the Russian Chemical Society, of the Moscow Meeting of Naturalists, of the St. Petersburg Academy, and Liebig's *Annalen*) on the same subject we only find applications of the same principles, which were afterwards confirmed by the labours of Roscoe, Carnelley, Thorpe, and others in England; of Rammelsberg (cerium and uranium), L. Meyer (the specific volumes of the elements), Zimmermann (uranium), and more especially of C. Winkler (who discovered germanium, and showed its identity with ekasilicon), and others in Germany; of Lecoq de Boisbaudran in France (the discoverer of gallium = ekaaluminium); of Clève (the atomic weights of the cerium metals), Nilson (discoverer of scandium = ekaboron), and Nilson and Pettersson (determination of the vapour density of beryllium chloride) in Sweden; and of Brauner (who investigated cerium, and determined the combining weight of tellurium = 125) in Austria, and Piccini in Italy.

I consider it necessary to state that, in arranging the periodic system of the elements, I made use of the previous researches of Dumas, Gladstone, Pettenkofer, Kremers, and Lenssen on the atomic weights of related elements, but I was not acquainted with the works preceding mine of De Chancourtois (*vis tellurique*, or the spiral of the elements according to their properties and equivalents) in France, and of J. Newlands (Law of Octaves—for instance, H, F, Cl, Co, Br, Pd, I, Pt form the first octave, and O, S, Fe, Se, Rh, Te, Au, Th the last) in England, although certain germs of the periodic law are to be seen in these works. With regard to the work of Prof. Lothar Meyer respecting the periodic law (notes 12 and 13), it is evident, judging from the method of investigation and from his statement (Liebig's *Annalen, Supt. Band* 7, 1870, 354), at the very commencement of which he cites my paper of 1869 above mentioned, that he accepted the periodic law in the form which I proposed.

In concluding this historical statement I consider it well to observe that no law of nature, however general, has been established all at once; its recognition is always preceded by many presentiments; the establishment of a law, however, does not take place when the first thought of it takes form, or even when its significance is recognised, but from 1 for hydrogen to 239 for uranium,[8a] given at the beginning of this book, is arranged in conformity with this law. This arrangement of the elements immediately shows that starting from the alkali metals, Li, Na, K, Rb, and Cs, the power of the elements to combine with oxygen at first increases uniformly with the atomic weight; for instance, in the series

Na, Mg, Al, Si, P, S, Cl,

the atomic weight gradually increases from 23 to 35·5, and the higher oxides are:

$$Na_2O,\ \underset{\displaystyle MgO}{\underset{\text{or}}{Mg_2O_2}},\ Al_2O_3,\ \underset{\displaystyle SiO_2}{\underset{\text{or}}{Si_2O_4}},\ P_2O_5,\ \underset{\displaystyle SO_3}{\underset{\text{or}}{S_2O_6}},\ Cl_2O_7.$$

When the element of group VII., giving R_2O_7, is reached, then either a new similar series begins after the element of the argon group (Chap. V.), so that, for example, after Cl and the argon series, we have:

K, Ca, Sc, Ti, V, Cr, Mn,

which again give the same types of oxides:

$$K_2O,\ \underset{\displaystyle CaO}{\underset{\text{or}}{Ca_2O_2}},\ Sc_2O_3,\ \underset{\displaystyle TiO}{\underset{\text{or}}{Ti_2O_4}},\ V_2O_5,\ \underset{\displaystyle CrO_3}{\underset{\text{or}}{Cr_2O_6}},\ Mn_2O_7,$$

or else the elements of group VII. continue as in the above instance, after Mn = 55 coming:

Ta = 56, Co = 59, and Ni = 59.

The most important points to be noticed here are that, as the atomic weight increases, (1) the series of the elements of a **small period** of seven groups from I. = R_2O to VII. = R_2O_7 periodically repeats itself,

---

only when it has been confirmed by the results of experiment, which the man of science must consider as the only proof of the correctness of his conjectures and opinions. I therefore, for my part, look upon Roscoe, De Boisbaudran, Nilson, Winkler, Brauner, Carnelley, Thorpe, and others who verified the adaptability of the periodic law to chemical facts as the true founders of the periodic law, the further development of which still awaits many fresh workers.

[8a] The atomic weights given in the tables at the beginning of this book have the values which follow from the theory of this subject explained in Chap. VII., and correspond with the sum of the existing (1902) data on this subject—assuming the atomic weight of oxygen to be conditionally 16. But in many portions of this book the fractions are neglected for the sake of brevity and simplicity; for instance, H is taken equal to 1 and not 1·008, Na = 23, and not 23·05, &c.; especially as, although these fractions have been confirmed for some of the elements (for instance, H, Na, N, Cl, &c.), they are not reliable for the majority. In such cases the atomic weights are given without fractions in the chief tables; for instance, Co = 59, I = 127.

and (2) a close resemblance exists between the properties of the elements of the **large periods** containing two small periods with the elements of group VIII. between the small periods and an element of the argon group at the end. As these last elements give no compounds, the group they form is known as the **zero group**[8b] because those elements which give the higher oxides, R_2O, and consequently salts RX, form the 1st group; the elements giving R_2O_2 or RO as their highest degree of oxidation belong to the 2nd group; those giving R_2O_3 as their highest oxides form the 3rd group, and so on. The large periods (K, Rb, Cs) beginning with the alkali metals, which give the most powerful alkalies, end with the halogens which correspond to the most powerful acids and contain intermediate elements with less distinctly marked chemical properties. The elements having the lowest atomic weights, although they bear the general properties of a group, still show many peculiar and independent properties.[9] Thus fluorine, as we saw, differs in many points from the other halogens, and lithium from the other alkali metals, and so on. These lightest elements may be termed

---

[8b] When the periodic system was first established (1869) not only were argon and its analogues, and their incapacity to enter into any of the ordinary forms of combination, unknown, but there were no reasons for even suspecting the existence of such elements. Now that the entire group, He, Ne, Ar, Kr, and Xe, is known, and also the fact that they evidently have as much in common as the group of the alkali metals or halogens, it must be admitted that they are as closely united together as either of these groups. This formed a sort of trial test for the theoretical side of the periodic law, like that put to it when beryllium was placed among the elements of group II. and not of group III. And as this test was successfully borne (for the oxide of beryllium corresponds in composition to the oxides of group II., as it should do, according to the law), so also the periodicity of the elements is in no way destroyed, but rather satisfied, by the argon elements, as explained in Chap. V., note 64. These elements, as Ramsay showed by their atomic weights in 1900, occupy a definite position between the halogens and alkali metals. They form their peculiar **zero group**, as explained in Chap. V., note 64. The necessity for a zero group was first recognised by Errera in Belgium. I consider it well to add that, judging from the incapacity of the elements of this group to enter into combination, the analogues of argon should be placed before the elements of group I., and that, according to the spirit of the periodic system, they should have smaller atomic weights than the alkali metals. This proved to be actually the case, and therefore gave a brilliant confirmation of the truth of the principles of periodicity, and clearly showed the true position held by the analogues of argon among the elements already known. Hence we are enabled to develop these principles more broadly than previously, and to look for the discovery of the zero group with atomic weights far smaller than that of hydrogen. So we may assume that an element of the zero group having an atomic weight 0·4 (perhaps it is Young's coronium) stands in the first series before hydrogen, and a limiting element with an infinitely small atomic weight, incapacity for chemical reaction, and exceedingly rapid motion of its (gaseous) molecules in the zero series of the zero group. Perhaps these properties should be ascribed to the atoms of universal all-penetrating ether. This idea is mentioned in the Preface of this book and also in a special article.

[9] This resembles the fact, well known to those having an acquaintance with organic chemistry, that in a series of homologues (Chap. VIII.) the first member (for instance, CH_4, CH_4O, CH_2O_2, &c.), in which there is the least carbon, although showing the general properties of the homologous series, presents also certain distinct peculiarities.

typical elements. They include, besides hydrogen (1st series), the 2nd and 3rd series; the 2nd begins with He and Li, the 3rd with Ne and Na, and they end with F and Cl. Thus, the alkali metals stand first here, as in the large periods, and the halogens at the end, which shows that these elements form special **small** periods:

H.
Li, Be, B, C, N, O, F.
Na, Mg . . .

In the annexed table all the remaining elements (excepting those rare elements—for instance, Pr, Nd, Sm, &c.—which have not yet been fully investigated, and the analogues of argon) are arranged according to *large periods.* In order to understand the essence of the matter, it must be remembered that here the atomic weight gradually increases along a given line; for instance, in the line commencing with K = 39 and ending with Br = 80, the intermediate elements have intermediate atomic weights, as is clearly seen in the tables given in the Preface, where the elements stand in the order of their atomic weights.

Even Series.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.			I.	II.	III.	IV.	V.	VI.	VII.
											Mg	Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Ce	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
—	—	—	Th	—	U											

Uneven Series.

In making use of the periodic system it is also useful to distinguish the *even* and *uneven* series in the large periods. The even series, beginning with the argon and alkali elements, gradually pass to the metals of group VIII., which are followed by the elements of the uneven series, ending with the true halogens, Cl, Br, I. In this manner the periodic system of the elements is fully expressed by arranging them in periods, series, and groups, as shown in the two tables given in the Preface of this book, which has been written entirely under the influence of the periodic system.

The same degree of analogy that we know to exist between potassium, rubidium, and cæsium; or chlorine, bromine, and iodine; or calcium, strontium, and barium, also exists between the elements of the other vertical columns. Thus, for example, zinc, cadmium, and mercury, which are described in the following chapter, present a very close analogy with magnesium.[9a]

[9a] A certain decrease in the number of analogues is observed in passing from group I. to group VIII. There are five analogues (H, Na, Cu, Ag, Au) in the uneven

For a true comprehension of the matter[10] it is very important to see that all the aspects of the distribution of the elements according to the

series of group I., four (Mg, Zn, Cd, Hg), in the same series of II., also four in groups III., IV., and V., but only three (S, Se, Te) in group VI., and the same number in groups VII. and VIII. Almost the same decrease is observed in the number of analogues of the even series. If an exceedingly light element (note 86) be recognised in the even series of the zero group, besides He, Ar, Kr, Xe, and Ne, this will also include five analogues; but the uneven series will only have two in the 1st and 3rd series. It is evident that of the typical elements of the small periods among the corresponding elements of the large periods only seven elements can be expected in the zero group, six (H, Li, Na, K, Rb, Cs) in group I., and less and less in the following groups; for instance, four in group VI. (O, S, Se, and Te) and only three in group VIII.

[10] Besides arranging the elements (*a*) in a successive order according to their atomic weights, with indication of their analogies by showing some of the properties—for instance, their power of giving one or another form of combination—both of the *elements* and of their compounds (as is done in the table at the end of Chap. XV. and in the Preface), (*b*) according to periods (as after the Preface), and (*c*) according to groups and series or small periods (as in the same tables), I am acquainted with the following methods of expressing the periodic relations of the elements: (1) *By a curve* drawn through points obtained in the following manner: The elements are arranged along the horizontal axis as abscissæ at distances from zero proportional to their atomic weights, whilst the values for all the elements of some property—for example, the specific volumes or the melting-points, are expressed by the ordinates. This method, although graphic, has the theoretical disadvantage that it does not in any way indicate the existence of a limited and definite number of elements in each period. There is nothing, for instance, in this method of expressing the law of periodicity to show that between magnesium and aluminium there can be no other element with an atomic weight of, say, 25, atomic volume 13, and in general having properties intermediate between those of these two elements. The actual periodic law does not correspond with a continuous change of properties, with a continuous variation of atomic weight—in a word, it does not express an uninterrupted function—and as the law is purely chemical, being based upon the conception of atoms and molecules which combine in multiple proportions, i.e., with intervals (not in all proportions), it depends *above all* on there being but few types of compounds which are arithmetically simple, *repeat themselves* and offer no uninterrupted transitions, so that each period can only contain a definite number of members. For this reason there can be no other elements between magnesium, which gives MgX_2, and aluminum, which forms AlX_3; there is a break in the continuity, according to the law of multiple proportions. The periodic law ought not, therefore, to be expressed by geometrical lines in which continuity is always understood, but rather in the manner of the theory of numbers—intermittently. Owing to these considerations I never have and never shall express the periodic relations of the elements by any geometrical figures. (2) *By a plane spiral.* Radii are traced from a centre, proportional to the atomic weights; analogous elements lie along one radius, and the points of intersection are arranged in a spiral. This method, adopted by De Chancourtois, Baumhauer, E. Huth, H. Erdmann, and others, has many of the imperfections of the preceding, although it removes the indefiniteness as to the number of elements in a period. It is merely an attempt to reduce the complex relations to a simple graphic representation, since the equation to the spiral and the number of radii are not dependent upon anything. (3) *By the lines of atomicity*, either parallel, as in Reynolds's and the Rev. S. Haughton's methods, or as in Crookes's method, arranged to the right and left of an axis, along which the magnitudes of the atomic weights are counted, and the position of the elements marked off, on the one side the members of the even series (para-magnetic, like oxygen, potassium, iron), and on the other side the members of the uneven series (diamagnetic, like sulphur, chlorine, zinc, and mercury). On joining up these points a periodic curve is obtained, compared by Crookes to the oscillations of a pendulum, and

order of their atomic weights express essentially one and the same

---

according to Haughton, representing a cubical curve. This method would be very graphic did it not require, for instance, that sulphur should be considered as bivalent and manganese as univalent, although neither of these elements gives stable derivatives of these types, and although the one is taken on the basis of the lowest possible compound SX_2 and the other on that of the highest, because manganese can be referred to the univalent elements only by the analogy of $KMnO_4$ to $KClO_4$. Furthermore, Reynolds and Crookes place hydrogen, iron, nickel, cobalt, and others outside the axis of atomicity, and consider uranium as bivalent without the least foundation. (4) Rantsheff endeavoured to classify the elements in their periodic relations by a system dependent on solid geometry. He communicated this mode of expression to the Russian Chemical Society, but his communication, which is apparently not void of interest, has not yet appeared in print. (5) *By algebraic formulæ*: for example, E. J. Mills (1886) endeavours to express all the atomic weights by the logarithmic function, $A = 15\ (n - 0{\cdot}9375t)$, in which the variables n and t are whole numbers. For instance, for oxygen $n = 2$ and $t = 1$, so that $A = 15{\cdot}94$; for antimony $n = 9$, $t = 0$, whence $A = 120$, and so on. n varies from 1 to 16, and t from 0 to 59. The analogues are hardly distinguishable by this method: thus for chlorine the magnitudes of n and t are 3 and 7, and for bromine, 6 and 6; for iodine 9 and 9; for potassium 3 and 14; for rubidium 6 and 18; for cæsium 9 and 20; but a certain regularity seems to be shown. One of the best attempts in this direction was made by J. H. Vincent (1902), who expressed the atomic weight, W, by the equation, $W = N^{1{\cdot}31}$, where N is a series of whole numbers from $N = 1$ for hydrogen to $N = 92$ for uranium. The periodicity is almost lost sight of in this case. It is interesting, however, and has the advantage of clearly showing the existence between the atomic weights of breaks like those between whole numbers. The same refers to Mr. Schönrock's (Nijnii Novgorod, 1896) endeavour to find a harmonic or other function corresponding with the atomic weights and analogies of the elements. For instance, $A + 20 \log A = 3n + 34$ gives the atomic weight, A, for $C = 12{\cdot}24$, if $n = 0$; $N = 14{\cdot}05$, if $n = 1$; $O = 15{\cdot}95$, if $n = 2$; $Mg = 24{\cdot}29$, if $n = 6$, &c. (6) A more natural method of expressing the dependence of the properties of elements on their atomic weights is obtained by *trigonometrical functions*, because this dependence is periodic, and therefore Rydberg in Sweden (1885) and F. Flavitzky (Kazan, 1887) have adopted a similar method of expression, which must be considered worthy of being worked out, although it does not express the absence of intermediate elements; for instance, between magnesium and aluminium, which is essentially the most important part of the matter. (7) The investigations of B. N. Tchitchérin (1888) are an effort in the latter direction. This author only studied the alkali metals, and discovered the following relation between their atomic volumes: $v = A(2 - 0{\cdot}0428An)$, where A is the atomic weight, and $n = 1$ for lithium and sodium, $\frac{4}{8}$ for potassium, $\frac{3}{8}$ for rubidium, and $\frac{2}{8}$ for cæsium. This endeavour offers many interesting points, but it does not concern the atomic weight, and the starting-point of the theory is the specific gravity of the metals at a definite temperature, and the specific gravity varies even under mechanical influences. (8) L. Hugo (1884) endeavoured to represent the atomic weights of Li, Na, K, Rb, and Cs by geometrical figures; for instance, $Li = 7$ represents a central atom $= 1$ and six atoms on the six terminals of an octahedron; Na is obtained by applying two such atoms on each edge of an octahedron, and so on. Such methods can hardly add anything new to our data respecting the atomic weights of analogous elements. The above review shows that the tendency to represent graphically the periodicity of the elements and express the atomic weights by an exact function has not yet led to the desired result. It is, moreover, clear that the most promising are those efforts to express the variation of the atomic weights by functions, like those given in paragraph (5), which give breaks or jumps corresponding with the change in nature of the elements. In this respect Armstrong adopted the most direct method (1902) of expressing the atomic weights by a series of whole numbers without fractions; but his method leads to no consequences beyond what the periodic system has already given.

fundamental **dependence—periodic properties.**[11] The following points must then be remarked in it :—

[11] Many natural phenomena exhibit a dependence of a periodic character. Thus the phenomena of day and night and of the seasons of the year, and vibrations of all kinds, exhibit variations of a periodic character in dependence on time and space. But in ordinary periodic functions one variable varies continuously, whilst the other increases to a limit, then a period of decrease begins and in turn reaches its limit, after which a period of increase again begins. It is otherwise in the periodic function of the elements. Here the mass of the elements does not increase continuously, but abruptly, by steps, as from magnesium to aluminium. So also the valency or atomicity leaps directly from 1 to 2 to 3, &c., without intermediate quantities, and in my opinion it is these properties which are the most important, and it is their periodicity which forms the substance of the periodic law. It *expresses the properties of the real elements*, and not of what may be termed their manifestations visually known to us. The external properties of elements and compounds are in periodic dependence on the atomic weight of the elements only because these external properties are themselves the result of the properties of the real elements which unite to form the 'free' elements and the compounds. To explain and express the periodic law is to explain and express the causes of the law of multiple proportions and of the differences between the elements, and the variation of their atomicity, and at the same time to understand what mass and gravitation are. It is generally thought that this is still premature. But just as without knowing the cause of gravitation it is possible to make use of the law of gravity, so for the aims of chemistry it is possible to take advantage of the laws discovered by chemistry without being able to explain their causes. The above-mentioned peculiarity of the laws of chemistry respecting definite compounds and the atomic weights leads one to think that the time has not yet come for their full explanation, and I do not think that it will come before the explanation of such a primary law of nature as the law of gravity.

It will not be out of place here to turn our attention to the many-sided correlation existing between the undecomposable **elements and the compound carbon radicles,** which has long been remarked (Pettenkofer, Dumas, and others), and reconsidered in recent times by Carnelley (1886), and most originally in Pelopidas's work (1883) on the principles of the periodic system. Pelopidas compares the series containing eight hydrocarbon radicles, C_nH_{2n+1}, C_nH_{2n}, &c.; for instance, C_6H_{13}, C_6H_{12}, C_6H_{11}, C_6H_{10}, C_6H_9, C_6H_8, C_6H_7, and C_6H_6, with the series of the elements arranged in eight groups. The analogy is particularly clear owing to the property of C_nH_{2n+1}, to combine with X, thus reaching saturation, and of the following members with X_2, X_3, . . . X_8, and especially because these are followed by an aromatic radicle—C_6H_5—in which, as is well known, many of the properties of the saturated radicle C_6H_{13}, and in particular the power of forming a univalent compound, are repeated. Pelopidas shows a confirmation of the parallel in the property of the above radicles of giving oxygen compounds corresponding with the groups in the periodic system. Thus the hydrocarbon radicles of the first group—for instance, C_6H_{13} or C_6H_5—give oxides of the form R_2O and hydroxides RHO, like the metals of the alkalies; and in the third group they form oxides R_2O_3 and hydrates RO_2H. For example, in the CH_3 series the corresponding compounds of the third group will be the oxide $(CH)_2O_3$ or $C_2H_2O_3$—that is, formic anhydride and the hydrate, CHO_2H, or formic acid. In the sixth group, with a composition of C_2, the oxide RO_3 will be C_2O_3, and hydrate $C_2H_2O_4$—that is, also a dibasic acid (oxalic) resembling, among the inorganic acids, sulphuric acid.

With respect to this remarkable parallelism, it must be observed that in the elements the atomic weight increases in passing to contiguous members of a higher valency, whilst here it decreases; but everything goes to prove that the periodic variability of elements and compounds is subject to some higher law whose nature, and cause, cannot at present be determined; and as the periodic law has only been generally recognised for a few years it is not surprising that any further progress towards its explanation can only be looked for in the development of facts touching on this subject.

1. The composition of the higher **oxygen compounds** is determined by the groups: the first group gives R_2O, the second R_2O_2 or RO, the third R_2O_3, &c. There are eight types of oxides, and therefore eight groups. Two series give a large period, and the same type of oxide is met with twice in a large period. For example, in the period beginning with potassium, oxides of the composition RO are formed by calcium and zinc, and of the composition RO_3 by chromium, selenium, &c. The oxides of the even series, of the same type, have stronger basic properties than the oxides of the uneven series, and the latter as a rule are endowed with an acid character. Therefore the elements which give exclusively bases, like the alkali metals, will be found at the commencement of the period, whilst such purely acid elements as the halogens will be at the end of the period. It must be observed that the acid character is, in the main, peculiar to the elements with small atomic weights in the uneven series, whilst the basic character is exhibited by the heavier elements in the even series. Hence elements which give acids predominate chiefly among the lightest (typical) elements, and more especially in the last groups; whilst the heaviest elements, even in the last groups (for instance, thallium, uranium) have a basic character. Thus the basic and acid characters of the higher oxides are determined (*a*) by the type of oxide, (*b*) by the even or uneven series, and (*c*) by the atomic weight. The groups are indicated by Roman numerals from I. to VIII.

2. **The hydrogen compounds,** being volatile or gaseous substances which are prone to reaction—such as HCl, H_2O, H_3N, and H_4C[12]—are only formed by the elements of the uneven series and higher groups giving oxides of the forms R_2O_7, RO_3, R_2O_5, and RO_2.

3. If an element gives a hydrogen compound, RX_m, it forms an **organo-metallic compound** of the same composition, where $X = C_nH_{2n+1}$, that is, the radicle of a saturated hydrocarbon. The elements of the uneven series, which are incapable of giving hydrogen compounds, and give oxides of the forms RX, RX_2, RX_3, also give organo-metallic compounds of this form proper to the higher oxides. Thus zinc forms the oxide ZnO, salts ZnX_2, and zinc ethyl $Zn(C_2H_5)_2$. The elements of the even series (large periods) form organo-metallic compounds with difficulty.

---

[12] The hydrides generalised by the periodic law are those to which metallo-organic compounds correspond, and are themselves either volatile or gaseous. The hydrogen compounds, like Na_2H, BaH_2, &c., are distinguished by other signs. They show (see end of last chapter) a systematic harmony, but they evidently should not be confused with true hydrides, any more than peroxides with saline oxides. Moreover, such hydrides have, like the peroxides, only recently been subjected to research, and have been but little studied.

4. The atomic weights of elements belonging to contiguous periods differ approximately by 45; for example, $K < Rb$, $Cr < Mo$, $Br < I$. But the elements of the typical series show much smaller differences. Thus the difference between the atomic weights of Li, Na, and K, between Ca, Mg, and Be, between Si and C, between S and O, and between Cl and F, is 16. As a rule, there is a greater difference between the atomic weights of two elements of one group and belonging to two neighbouring series ($Ti - Si = V - P = Cr - S = Mn - Cl = Nb - As$, &c. $= 20$); and this difference attains a maximum with the heaviest elements (for example, $Th - Pb = 26$, $Bi - Ta = 26$, $Ba - Cd = 25$, &c.). Thus even in the magnitude of the differences of the atomic weights of analogous elements there is observable a certain connection with the gradation of their properties.[12a]

5. According to the periodic system every element occupies a certain position, determined by the group (indicated in Roman numerals) and series (Arabic numerals) in which it occurs. These indicate the atomic weight, the analogues, properties, and type of the higher oxide, and of the hydrogen and other compounds—in a word, all the chief quantitative and qualitative features of an element, although there yet remain a whole series of further details and peculiarities, the cause of which should perhaps be looked for in small differences of the atomic weights. If in a certain group there occur elements, R_1, R_2, R_3, and if in that series which contains one of these elements, for instance R_2, an element Q_2 precedes it and an element T_2 succeeds it, then the properties of R_2 are determined by the mean of the properties of R_1, R_3, Q_2, and T_2. Thus, for instance, the atomic weight of $R_2 = \frac{1}{4}(R_1 + R_3 + Q_2 + T_2)$. For example, selenium occurs in the same group as sulphur, $S = 32$, and tellurium, $Te = 127$, and, in the 7th series, $As = 75$ stands before it and $Br = 80$ after it. Hence the atomic weight of selenium should be $\frac{1}{4}(32 + 127 + 75 + 80) = 78{\cdot}5$, which is near to that generally accepted, $Se = 79$, in which there is a possible error in the first decimal,

---

[12a] The relation between the atomic weights, and especially the difference of 16, was observed in the sixth and seventh decades of the last century by Dumas, Pettenkofer, L. Meyer, and others. Thus Lothar Meyer in 1864, following Dumas and others, grouped together the tetravalent elements carbon and silicon; the trivalent elements nitrogen, phosphorus, arsenic, antimony, and bismuth; bivalent oxygen, sulphur, selenium, and tellurium; univalent fluorine, chlorine, bromine, and iodine, and the univalent metals lithium, sodium, potassium, rubidium, cæsium, and thallium. The first germs of the periodic law are visible in such observations as these. Since its establishment this subject has been most fully worked out by Rydberg, who observed a periodicity in the variation of the differences between the atomic weights of two contiguous elements, and its relation to their atomicity (see Chap. XIV., note 9). A. Bazaroff (1887) investigated the same subject, taking, not the arithmetical differences of contiguous and analogous elements, but the ratio of their atomic weights; and he also observed that this ratio alternately rises and falls as the atomic weights increase.

so that 78·5 may be nearer the actual figure. Other properties of selenium may also be determined in this manner; for example, arsenic forms H_3As, bromine gives HBr, and it is evident that selenium, which stands between them, should form H_2Se, with properties intermediate between those of H_3As and HBr. Even the physical properties of selenium and its compounds, not to speak of their composition, being determined by the group in which it occurs, may be foreseen with a close approach to reality from the properties of sulphur, tellurium, arsenic, and bromine. **In this manner it is possible to foretell the properties of elements still unknown**, especially when it is surrounded by well-known elements. For instance, in the position, IV, 5—that is, in the IVth group and 5th series—an element is still wanting. These unknown elements may be named after the preceding known element of the same group by adding to the first syllable the prefix *eka-*, which means *one* in Sanskrit. The element IV, 5, follows after IV, 3, and this latter position being occupied by silicon, I named this formerly unknown element ekasilicon and its symbol Es. The following are the properties which this element should have on the basis of the known properties of silicon, tin, zinc, and arsenic. Its atomic weight is nearly 72, it forms a higher oxide EsO_2, a lower oxide EsO, compounds of the general form EsX_4, and chemically unstable lower compounds of the form EsX_2. Es gives volatile organo-metallic compounds; for instance, $Es(CH_3)_4$, $Es(CH_3)_3Cl$, and $Es(C_2H_5)_4$, which boil at about 160°, &c.; also a volatile and liquid chloride, $EsCl_4$, boiling at about 90° and of specific gravity about 1·9. EsO_2 will be the anhydride of a feeble colloidal acid, metallic Es will be rather easily obtainable from the oxides and from K_2EsF_6 by reduction, EsS_2 will resemble SnS_2 and SiS_2, and will probably be soluble in ammonium sulphide; the specific gravity of Es will be about 5·5, and EsO_2 will have a density of about 4·7, &c. Such a prediction of the properties of ekasilicon was made by me in 1871, on the basis of the properties of the elements analogous to it; namely, IV, 3 = Si, IV, 7 = Sn, and also II, 5 = Zn and V, 5 = As. And now that this element has been discovered by C. Winkler, of Freiberg, Saxony, it has been found that its actual properties entirely correspond with those which were foretold, as was stated by Winkler in his excellent research on germanium.[13] In this we see a most

---

[13] The laws of nature admit of no exceptions, and in this they clearly differ from such rules and maxims as are found in grammar, and in other inventions, methods, and relations of man's creation. The confirmation of a law is only possible by deducing consequences from it, such as could not possibly be foreseen without it, and by verifying those consequences by experiment and further proofs. Therefore, when I perceived the periodic law, I (1869–1871, note 9) deduced such logical consequences from it as could serve to show whether it were true or not. Among them were the prediction of the

important confirmation of the truth of the periodic law. This element, now called germanium, Ge (see Chap. XVIII.), is not the only one that has been predicted by the periodic law.[14] We shall see in describing the elements of the third group that properties were foretold of an element ekaaluminium, III, 5, El = 68, and were afterwards verified when the metal termed 'gallium' was discovered by Lecoq de Boisbaudran. So also, according to Nilson, the properties of scandium corresponded with those predicted for ekaboron.

6. As a true law of nature is one to which there are no exceptions, the periodic dependence of the properties on the atomic weights of the elements gives a **new means for determining** by the equivalent **the atomic weight** or atomicity of imperfectly investigated but known elements, for which no other means could as yet be applied for determining the true atomic weight. At the time (1869) when the periodic

properties of undiscovered elements and the correction of the atomic weights of many, at that time little known, elements. Thus uranium was considered as trivalent, U = 120; but as such it did not correspond with the periodic law. I therefore proposed to double its atomic weight—U = 240—and the researches of Roscoe, Zimmermann, and others justified this alteration (Chap. XXI.). It was the same with cerium (Chap. XVIII.), whose atomic weight it was necessary to change according to the periodic law. I therefore determined its specific heat, and the result I obtained was verified by the new determinations of Hillebrand. I then corrected certain formulæ of the cerium compounds, and the researches of Rammelsberg, Brauner, Cleve, and others verified the proposed alterations. It was necessary to do one thing or the other—either to consider the periodic law as completely true, and as forming a new instrument in chemical research, or to refute it. Acknowledging the method of experiment to be the only true one, I myself verified what I could, and gave everyone the possibility of proving or confirming the law, and did not think, like L. Meyer (Liebig's *Annalen*, *Supt. Band* 7, 1870, 364), when writing about the periodic law, that 'it would be rash to change the accepted atomic weights on the basis of so uncertain a starting-point.' ('Es würde voreilig sein, auf so unsichere Anhaltspunkte hin eine Aenderung der bisher angenommenen Atomgewichte vorzunehmen.') In my opinion, the *basis* offered by the periodic law had to be verified or refuted, and experiment in every case verified it. The starting-point then became general. No law of nature can be established without such a method of testing it. Neither De Chancourtois, to whom the French ascribe the discovery of the periodic law, nor Newlands, who is put forward by the English, nor L. Meyer, who is now cited by many as its founder, ventured to foretell the *properties of undiscovered* elements, or to alter the 'accepted atomic weights,' or, in general, to regard the periodic law as a new, strictly established law of nature, as I did from the very beginning (1869).

[14] When in 1871 I wrote a paper on the application of the periodic law to the determination of the properties of hitherto undiscovered elements, I did not think I should live to see the verification of this consequence of the law, but such was to be the case. Three elements were described—ekaboron, ekaaluminium, and ekasilicon—and now, after the lapse of twenty years, I have had the great pleasure of seeing them discovered and named Gallium, Scandium, and Germanium, after those three countries where the rare minerals containing them are found, and where they were discovered. For my part I regard L. de Boisbaudran, Nilson, and Winkler, who discovered these elements, as the true corroborators of the periodic law. Without them it would not have been accepted to the extent it now is. So also I consider that Prof. Ramsay has corroborated the periodic law by having discovered He, Ne, Ar, Kr, and Xe, and determined their atomic weights, which fully satisfy the requirements of the periodic system of the elements.

law was first proposed there were several such elements. It thus became possible to learn their true atomic weights, and these were verified by later researches. Among the elements thus concerned were indium, uranium, cerium, yttrium, and others.[15]

7. The periodic variability of the properties of the elements in dependence on their masses presents a distinction from other kinds of periodic dependence (as, for example, the sines of angles vary periodically and successively with the growth of the angles or the temperature of the atmosphere with the course of time—daily or yearly), in that the weights of the atoms do not increase gradually, but by leaps; that is, according to the laws of periodicity and multiple proportions (Dalton's), there not only are not, but there cannot be, any transition or intermediate elements between two neighbouring ones (for example, between K=39 and Ca=40, or Al=27 and Si=28, or C=12 and N=14, &c.). Just as in a molecule of a hydrogen compound there may be either one, as in HF, or two, as in H_2O, or three, as in NH_3, &c., atoms of hydrogen to an atom of another element; but as there

---

[15] Taking indium, which occurs together with zinc, as our example, we shall show the principle of the method employed. The equivalent of indium to hydrogen in its oxide is 37·7—that is, if we suppose its composition to be like that of water; then In = 37·7, and the oxide of indium is In_2O. The atomic weight of indium was taken as double the equivalent—that is, indium was considered to be a bivalent element—and In = 2 × 37·7 = 75·4. If indium only formed an oxide, RO, it should be placed in group II. But in this case it appears that there would be no place for indium in the system of the elements, because the positions II., 5 = Zn = 65 and II., 6 = Sr = 87 were already occupied by known elements, and according to the periodic law an element with an atomic weight 75 could not be bivalent. As neither the vapour density nor the specific heat, nor even the isomorphism (the salts of indium crystallise with great difficulty) of the compounds of indium was known, there was no reason for considering it to be a bivalent metal, and therefore it might be regarded as trivalent, quadrivalent, &c. If it be trivalent, then In = 3 × 37·7 = 113, and the composition of the oxide is In_2O_3 and that of its salts InX_3. In this case it at once falls into its place in the system, namely, in group III. and series 7, between Cd = 112 and Sn = 118, as an analogue of aluminium or dvialuminium (dvi = 2 in Sanskrit). All the properties observed in indium correspond with this position; for example, the density, cadmium = 8·6, indium = 7·4,' tin = 7·2; the basic properties of the oxides CdO, In_2O_3, SnO_2, vary regularly, so that the properties of In_2O_3 are intermediate between those of CdO and SnO_2 or Cd_2O_2 and Sn_2O_4. That indium belongs to group III. has been confirmed by the determination of its specific heat (0·057 according to Bunsen, and 0·055 according to me) and also by the fact that, like aluminium, indium forms alums, and therefore belongs to the same group.

Similar considerations necessitated taking the atomic weight of titanium as nearly 48, and not as 52, the figure derived from many analyses. And these corrections, made on the basis of the law, have also been confirmed, for Thorpe found, by a series of careful experiments, the atomic weight of titanium to be that foreseen by the periodic law. Notwithstanding that previous analyses gave Os = 199·7, Ir = 198, and Pt = 187, the periodic law shows, as I remarked in 1871, that the atomic weights should rise from osmium to platinum and gold, and not fall. Many researches, and especially those of Seubert, have fully verified this statement, based on the law. Thus a true law of nature anticipates facts, foretells magnitudes, gives a hold on nature, and leads to improvements in the methods of research, &c.

cannot be molecules containing $2\frac{1}{2}$ atoms of hydrogen to one atom of another element, so, according to the periodic law, there cannot be any element intermediate between N and O, with an atomic weight greater than 14 or less than 16, or between K and Ca. Hence the periodic dependence of the elements cannot be expressed by any continuous algebraical function in the same way that it is possible, for instance, to express the variation of the temperature during the course of a day or year.

8. The essence of the notions giving rise to the periodic law consists in a general physico-mechanical principle which recognises the correlation, transmutability, and equivalence of the forces of nature. Gravitation, attraction at small distances, and many other phenomena are in direct dependence on the mass of matter. It might therefore have been expected that chemical forces would also depend on mass. A dependence is in fact shown, the properties of elements and compounds being determined by the masses of the atoms of which they are formed. The weight of a molecule, or its mass, determines, as we have seen (Chap. VII. and elsewhere), many of its properties independently of its composition. Thus carbonic oxide, CO, and nitrogen, N_2, are two gases having the same molecular weight, and many of their properties (density, liquefaction, specific heat, &c.) are similar or nearly similar. The differences dependent on the nature of a substance play another part, and form magnitudes of another order. But *the properties of atoms are mainly determined by their mass* or weight, and are in dependence upon it.[15a] As the mass increases the properties vary, at

---

[15a] I have often been asked on what basis, and from what standpoint of thought, I discovered the periodic law which I defend so stubbornly. The following is the best answer I can give. Of the exact nature of matter we have no knowledge. The dynamic philosophers of old and some modern spiritualists who have meditated on this subject and have come to the conclusion that our conception of matter is entirely based upon impressions produced by phenomenal forces and forms of motion have either almost entirely denied the independent nature or existence of matter, or else have so far subjected it to the conception of force (energy) that they admit the creation of matter from force, although they do not recognise the reverse. Thought, which has no resting-place in the history of knowledge, is free to wander in these unlimited regions whither and how it pleases, and may therefore return to the point from which it started in the dawn of science. I do not in the least censure such thought in any respect, but when my thoughts turn to this region they always rest steadfastly on the fact that we are unable to comprehend matter, force, and the soul in their substance or reality, but are only able to study them in their manifestations in which they are inevitably united together, and that beyond their inherent indestructibility they also have their tangible, common, peculiar signs or properties which should be studied in every possible aspect. The results of my labours in the study of matter show me two such signs or properties in matter: (1) the *mass* which occupies space and evinces itself in gravity or more clearly and really in weight, and (2) the *individuality* expressed in chemical transmutations and most clearly formulated in the notion of the chemical elements. In thinking of matter outside any idea of material atoms, it is impossible for me to exclude two

first successively and regularly, and then return to their original magnitude and commence a fresh period of variation like the first. Nevertheless, here as in other phenomena, there are cases in which a small variation of the mass of the atom leads to a small variation of properties, and determines differences of a second order. This is seen, for instance, in group VIII., which is treated more fully in Chapters XXII. and XXIII.; thus the atomic weights of cobalt and nickel, of rhodium, ruthenium, and palladium, and of osmium, iridium, and platinum, are very close to each other, and their properties are also very much alike, the differences being hardly perceptible. And if the properties of atoms are a function of their weight, many ideas which have more or less rooted themselves in chemistry must be developed and worked out in the sense of this deduction. Although at first sight it appears that the chemical elements are perfectly self-existent in their character, and completely independent of each other, yet this idea of the nature of the elements must now be replaced by the notion of the dependence of their properties upon *their mass*; that is to say, the subjection of the individuality of the elements to a common higher principle which evinces itself in gravity and in the majority of physico-chemical phenomena. Many chemical deductions then acquire a new sense and significance, and a regularity is observed where it would otherwise escape attention.

9. This is particularly apparent in the physical properties to the consideration of which we shall afterwards turn, and we will now point out that first Gustavson (Chap. X., note 28) and subsequently Potilitzin (Chap. XI., note 66) demonstrated the dependence of purely reactive powers on the atomic weight and on that fundamental property which is expressed in the forms of their compounds, whilst in a number of other cases the purely chemical relations of elements proved to be in connection with their periodic properties. As a case in point, it may be

questions: How much and what kind of matter? Which qualities correspond to the conceptions of mass and of the chemical elements? And the history of the science of matter, that is, of chemistry, inevitably compels us to recognise the indestructibility not only of matter but also of the chemical elements. Therefore the thought involuntarily arises that there must be some bond of union between mass and the chemical elements; and as the mass of a substance is ultimately expressed (although not absolutely, but only relatively) in the atom, a functional dependence should exist and be discoverable between the individual properties of the elements and their atomic weights. But nothing, from mushrooms to a scientific dependence, can be discovered without looking and trying. So I began to look about and write down the elements with their atomic weights and typical properties, analogous elements, and like atomic weights on separate cards, and this soon convinced me that the properties of the elements are in periodic dependence upon their atomic weights; and although I have had my doubts about some obscure points, yet I have never once doubted the universality of this law, because it could not possibly be the result of chance.

mentioned that Carnelley remarked a dependence of the decomposability of the hydrates on the position of the elements in the periodic system; whilst L. Meyer, Willgerodt, and others established a connection between the atomic weight or the position of the elements in the periodic system and their property of serving as media in the transference of the halogens to the hydrocarbons.[16] Bailey pointed out a periodicity in the stability (under the action of heat) of the oxides, namely: (*a*) in the even series (for instance, CrO_3, MoO_3, WO_3, and UO_3) the higher oxides of a given group decompose with greater ease the smaller the atomic weight, whilst in the uneven series (for example, CO_2, GeO_2, SnO_2, and PbO_2) the contrary is the case; and (*b*) the stability of the higher saline oxides in the even series (as in the fourth series from K_2O to Mn_2O_7) decreases in passing from the lower to the higher groups, while in the uneven series it increases from the group I. to IV. and then falls from IV. to VII.; for instance, in the series Ag_2O, CdO, In_2O_3, SnO_2, and then SnO_2, Sb_2O_5, TeO_3, I_2O_7. K. Winkler looked for and actually found (1890) a dependence between the reducibility of the metals by magnesium and their position in the periodic system of the elements, &c. The greater the attention paid to this field the more often is a distinct connection found between the variation of purely chemical properties of analogous substances and the variation of the atomic weights of the constituent elements and their position in the periodic system. Further, since the periodic system has become more firmly established, many facts have been gathered, showing that there are many similarities between Sn and Pb, B and Al, Cd and Hg, &c., which, although foreseen in some cases, had not been previously observed, and are a consequence of the periodic law. Keeping our attention in the same direction, we see that the most widely distributed elements in nature are those with small atomic weights; in organisms the lightest elements exclusively predominate (hydrogen, carbon, nitrogen, oxygen), the small mass of which facilitates those transformations peculiar to organisms. Poluta (of Kharkoff), C. C. Botkin, Blake, Brenton, and

---

[16] Meyer, Willgerodt, and others, guided by the fact that Gustavson and Friedel had remarked that metalepsis proceeds rapidly in the presence of aluminium, investigated the action of nearly all the elements in this respect. For example, they took benzene, added to it the metals to be experimented on, and passed chlorine through the liquid in diffused light. When, for instance, sodium, potassium, barium, &c., are taken, there is no action on the benzene; that is, hydrochloric acid is not disengaged. But if aluminium, gold, or, in general, any metal having this power of aiding chlorination (*Halogenüberträger*) is employed, the action is then clearly seen from the volumes of hydrochloric acid evolved (especially if the metallic chloride formed is soluble in benzene). Thus, in group I., and in general among the even and light elements, there are none capable of serving as agents of metalepsis; but aluminium, gallium, indium, antimony, tellurium, and iodine, which are contiguous members in the periodic system, are excellent transmitters (carriers) of the halogens.

others even discovered a correlation between the physiological action of salts and other reagents on organisms and the positions occupied in the periodic system by the metals contained in them. Nobody thought of looking for such relations before the periodic law was established; a fact which proves it to be a natural and true law. A portion of the veil hiding the nature of the simple bodies has been to some extent raised by the periodic law.[16a]

[16a] The long-forgotten 'idea' of a primary matter from which all the simple bodies are supposed to have originated has been more and more frequently brought forward as the periodic law has taken root. This appears to me to be perfectly natural if mass be considered as directly dependent upon the quantity of a substance as is the case in mechanics. Before discussing this opinion—the composition of the atoms of simple bodies from the atoms of primary matter—I think it necessary to draw attention to the fact that the conception of mass is derived exclusively from gravity or weight, that is, from the action of forces and the study of motions. At the present day we have every right to say that different forces act on a substance in conformity with the action of gravity on it, but nothing tells us that we therefore (from the weight) know the quantity of matter in the substance; for Newton and Bessel's experiments, which showed that pendulums of equal lengths and equal weights vibrate in equal periods of time, although they be of different material (and also the similar experiments with horizontal 'torsion' pendulums), only prove that the action of the forces in the weighings and vibrations of the pendulums are equal and almost similar in all respects, but they do not explain the conception of the quantity of matter; this remains a conditional silent compromise recognising that the weight or mass is proportional to the quantity of matter, or else, according to the notion of a primary form of matter, proportional to the number of atoms of this primary matter. For my part I have not the slightest wish to unsettle the fruitful doctrine of mass, but only desire to point out that if chemical doctrines had been developed before physico-mechanical ones, the atomic quantities of simple bodies might have been regarded as perfectly independent in their nature, and as acting according to their weight in all their chemical and also physico-mechanical relations, that is, that masses which are similar in a mechanical sense do not contain similar quantities of a substance, while masses with a similar amount of a substance, that is, with a similar number of different atoms, do not act similarly in a physico-mechanical sense (i.e., at certain distances), but according, and in proportion, to their inherent peculiarities, which are retained both when the atoms form simple bodies and when they enter into different combinations. By this I only wish to say that for me the conceptions of the chemical elements and what (beyond any atomic theory) we consider as their atomic weights belong to those primary conceptions of all natural science, like those of mass or quantity of matter, and I think that in the future when chemistry shall have reached the age of mechanics (there is a difference of almost two centuries, and the more youthful chemistry is growing more rapidly than mechanics), some kind of compromise will be arrived at, and the quantity of a substance will be calculated in a manner quite different from the present one, although the conceptions of mass and atomic weight will be retained.

It was necessary that I should give the above general considerations in order to explain my personal views on the question of the formation of the simple bodies from a supposed primary form of matter. I cannot refute it, but it is still more impossible for me to accept it, for there are at the present day no sound bases for supporting such a view. And as experiment so far denies the possibility of transmuting the elements into each other, and in no wise explains the chemical nature of the ether and its transition into matter, it appears to me that the whole question of a primary matter belongs to the province of fancy and not of science, and I do not recommend any beginning to study chemistry—and this book is designed for such—to occupy themselves with it.

10. When (1869–1871) the periodic law was first established, such very inactive elements, in a chemical sense, as the analogues of argon (He, Ne, Kr, and Xe) were utterly unknown and could not be foreseen. Hence the position they occupied among the other elements offered a most important means for strengthening the conceptions of this law. And indeed, judging from the fact that the argon elements do not enter into combination, they should, according to the periodic law, be placed in a zero group, that is, before group I., and they should therefore have smaller atomic weights than the elements of this group (see Chap. V., note 64).

11. As, from the necessity of the case, the physical properties of the elements and compounds must be in dependence on the composition of a substance, i.e., on the quality and quantity of the elements forming it, so for them also must be expected a dependence on the atomic weight of the component elements, and consequently also on their periodic distribution.[17] We shall meet with repeated proofs of this in the further exposition of our treatise, and for the present will content ourselves with citing the discovery by Errera (Belgium) in 1878 and by Carnelley in 1879 of the dependence of the magnetic properties of the elements on the position occupied by them in the periodic system. They showed that all the elements of the *even series* (beginning with lithium, potassium, rubidium, cæsium) belong to the class of *magnetic* (paramagnetic) substances; for example, according to Faraday and others,[17a] C, O, Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Nb, Mo, Ru, Rh, Pd, Ba, La, Ce, W, Os, Ir, Pt, Th, U, are magnetic; and the elements of the *uneven series are diamagnetic*, H, Na, P, S, Cl, Cu, Zn, Se, Br, Ag, Cd, Sb, Te, I, Au, Hg, Tl, Pb, Bi. Carnelley also showed that the **melting-point** of elements varies periodically, as is seen by the figures

---

[17] The periodic relations enumerated above appertain to the real elements, and not to the elements in the free state as we know them; and it is very important to note this, because the periodic law refers to the real elements, inasmuch as the atomic weight is proper to the real element, and not to the 'free' element, to which, as to a compound, a molecular weight is proper. Physical properties are chiefly determined by the properties of molecules, and only indirectly depend on the properties of the atoms forming the molecules. For this reason the periods, which are clearly and quite distinctly expressed—for instance, in the forms of combination—become to some extent involved (complicated) in the physical properties of their members. Thus, for instance, besides the *maxima* and *minima* corresponding with the periods and groups, new molecules appear; for example, as regards the melting-point of germanium, a local *maximum* appears, which was, however, foreseen by the periodic law when the properties of germanium (ekasilicon) were forecast.

[17a] The relation of certain elements (for instance, the analogues of Pt) among diamagnetic and paramagnetic bodies is sometimes doubtful (probably owing partly to the imperfect purity of the reagents under investigation). This subject was studied in some detail by Bachmetieff in 1889.

in the accompanying table (last column) [18] where all the most trustworthy data are collected, predominance being given to those having maximum and minimum values.[19]

---

[18] It is evident that many of the temperatures, especially those exceeding 1000°, have been determined with but little exactitude, and some, placed in the accompanying table with the sign (?), I have only given on the basis of rough and comparative determinations, calculated from the melting-points of silver and platinum, now established by many observers. Judging by this table, besides the large periods whose maxima correspond with carbon, silicon, vanadium, manganese, and osmium, there are also small periods in the melting-points, and their maxima correspond with Ge, Te. The minima correspond with the halogens and metals of the alkalies. A distinct periodicity is also seen in the coefficients of linear expansion (chiefly according to Fizeau); for instance, in the vertical series (according to the magnitude of the atomic weight), Fe, Co, Ni, Cu, the linear expansions in millionths of an inch are 12, 13, 17, and 29; for Rh, Pd, Ag, Cd, In, Sn, and Sb the coefficients are 8, 12, 19, 31, 46, 26, and 12, so that a maximum is reached at In. In the series Ir (7), Pt (5), Au (14), Hg (60), Tl (31), Pb (29), and Bi (14), the maximum is at Hg and the minimum at Pt. Raoul Pictet expressed this connection by the product $a(t+273)\sqrt[3]{A/d}$, which he found to be nearly constant for all elements in the free state, and equal to about 0·045, a being the coefficient of linear expansion, $t+273$, the melting-point calculated from the absolute zero ($-273°$), and $\sqrt[3]{A/d}$, the mean distance between the atoms, if A is the atomic weight and d the sp. gr. of an element. Although the above product is not strictly constant, nevertheless Pictet's rule gives an idea of the bond between magnitudes which ought to have a certain connection with each other. De Heen, Nadeschdin, and others also studied this dependence, but their deductions do not give a general and exact law. Further details must be sought in works on physical chemistry. But I think it necessary to add that many often seek for physical properties a dependence upon the specific volumes, and this dependence may always be transferred to one upon the atomic weights, because the specific volumes are themselves functions of the atomic weights.

[19] Carnelley found a similar dependence on comparing the melting-points of the metallic chlorides, many of which he redetermined for this purpose. The melting-points (and boiling-points, in brackets) of the following chlorides are known, and a certain regularity is seen to exist in them, although the number (and degree of accuracy) of the data is insufficient for a generalisation:—

LiCl 598°	$BeCl_2$ 600°	BCl_3 −20°
NaCl 772°	$MgCl_2$ 708°	$AlCl_3$ 187°
KCl 784°	$CaCl_2$ 719°	$ScCl_3$?
CuCl 434° (993°)	$ZnCl_2$ 262° (680°)	$GaCl_3$ 76° (217°)
AgCl 451°	$CdCl_2$ 541°	$InCl_3$?
TlCl 427° (713°)	$PbCl_2$ 498° (908°)	$BiCl_3$ 227°

Laurie (1882) also observed a periodicity in the **quantity of heat** developed in the formation of the chlorides, bromides, and iodides (fig. 89). This is seen from the following figures, which express the heat developed in thousands of calories, and referred to a molecule of chlorine, Cl_2, so that the heat of formation of KCl is doubled, and that of $SnCl_4$ halved, &c.: Na 195 (Ag 59, Au 12), Mg 151 (Zn 97, Cd 93, Hg 63), Al 117, Si 79 (Sn 64), K 211 (Li 187), Ca 170 (Sr 185, Ba 194). Hence the greatest amount of heat is evolved by the metals of the alkalies, and in each period the heat evolution falls from them to the halogens, which evolve very little heat in combining together. Richardson, by comparing the heats of formation of the fluorides, also came to the conclusion that they are in periodic dependence upon the atomic weights of the combined elements.

In this respect it may not be superfluous to remark: (1) that Thomsen, whose results

12. A. A. Baikoff (1902, a communication made to me), in his researches on many copper alloys, and guided by already existing data, came to the conclusion that copper follows the periodic system of the elements in its alloys of definite composition. That is, it behaves as an element of group I. like hydrogen. Thus its higher definite and characteristic alloys and compounds which contain the greatest proportion of copper have a composition MCu_2 with the elements of group II., belonging to the uneven series; MCu_3 for group III., MCu_4 for group

---

I have employed above, observed a correlation in the calorific equivalents of analogous elements, although he did not remark their periodic variation; (2) that the uniformity of many thermochemical deductions must gain considerably by the application of the periodic law, which evidently repeats itself in calorimetric data; and that these data frequently lead to true forecasts is due to the periodicity of the thermal as well as of many other properties, as was remarked by Laurie; and (3) that the heat of formation of the oxides is also subject to a periodic dependence which differs from that of the heat of formation of the chlorides in that the greatest quantity corresponds with the bivalent metals of the alkaline earths (magnesium, calcium, strontium, barium), and not with the univalent metals of the alkalies, as is the case with chlorine, bromine, and iodine. This circumstance is probably connected with the fact that chlorine, bromine, and iodine are univalent elements, and oxygen bivalent (compare, for instance, Chap. XI., note 13, Chap. XXII., note 40, Chap. XXIV., note 28a, &c.).

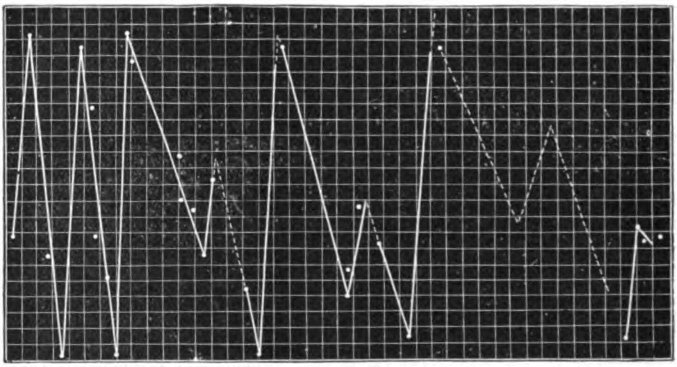


FIG. 89.—Laurie's diagram for expressing the periodic variation of the heat of formation of the chlorides. The abscissæ give the atomic weights from 0 to 210, and the ordinates the amounts of heat from 0 to 220 thousand calories evolved in the combination with Cl_2 (i.e., with 71 parts of chlorine). The apices of the curve correspond to Li, Na, K, Rb, Cs, and the lower extremities to F, Cl, Br, and I.

Lecoq de Boisbaudran, Rydberg, Ramage (Chap. XVII., note 27), Hartley, Keyser, and others, in investigating the spectra of the alkali metals and metals of the alkaline earths, &c., came to the conclusion that in this respect also there is a regularity of a periodic character in dependence upon the atomic weights. Probably a closer and systematic study of many of the properties of the elements and of complex and simple bodies formed by them will lead more and more frequently to similar conclusions, and to an extension of the range of application of the periodic law; such, for instance, as the refractive index, cohesion, ductility, and similar properties of corresponding compounds or of the elements themselves. Much has already been done in this respect, and details will be found in works on physical chemistry.

IV., MCu_3 for group V., MCu_2 for group VI., and MCu for VII. The following grouping of the most reliable cases explains this relation for the compounds of Cu, Ag, Na, and H:—

Group II. Cu_2Mg, Cu_2Zn, Cu_2Cd, Ag_2Zn, Ag_2Cd, Na_2Hg.
„ III. Cu_3Al.
„ IV. Cu_4Sn, H_4Si (and also Mg_2Sn, Al_4Sn_3).
„ V. Cu_3Sb, Ag_3Sb, Na_3Bi, H_3Sb.
„ VI. Cu_2S, Cu_2O, Ag_2O, H_2S.
„ VII. CuCl, CuI, HCl.

Thus the compositions of bronze (Cu + Sn), judging by the alloy Cu_4Sn, of brass (Cu + Zn), judging by the alloy Cu_2Zn, of aluminium bronze, judging by the alloy Cu_2Al and of the characteristic alloy Cu_3Sb, indicate a perfect analogy between the compounds of copper and chlorine Cl_4Sn, Cl_2Zn, Cl_3Al, and Cl_3Sb.[19a] This is all the more remarkable because alloys in their analogy to solutions belong to the class of so-called indefinite compounds, in which many recognise the predominance of purely physico-mechanical agencies. It may be hoped that the application of the principle of periodicity noted by Baikoff will prove universal when different alloys have been carefully investigated in this light,[19b] and that this method will give a new bond of a

[19a] In a letter to me dated September 27, 1902, Mr. Baikoff concludes his remarks on the applicability of the periodic system to alloys, with the following words:—

'The metallic compounds which correspond by the forms of their combination to the periodic law must be regarded as the most characteristic compounds. Thus with many combinations of metals forming several definite compounds, the relation between the higher (in Cu) form and the others is just like that between an anhydrous salt and its crystallohydrates. Examples of this kind are seen in the compounds $SnCu_4$ and $SnCu_3$ and $SbCu_3$ and $SbCu_2$. Here the lower forms ($SnCu_3$ and $SbCu_2$) stand to their higher forms exactly like $Na_2SO_4,10H_2O$, for instance, which melts in its water of crystallisation with the separation of the anhydrous salt. It is, moreover, remarkable that the external properties of these lower forms are more characteristic than those of the higher forms; for instance, $SbCu_2$ is violet in colour. This also recalls what we see in salts, where we frequently meet with instances in which the most characteristic form is not the simplest fundamental, but the more complex, form, as is seen, for example, in the crystallohydrates, e.g., $CuSO_4,5H_2O$, &c. The dimorphism of the fundamental typical forms of the metallic compounds is characteristic. It is undoubted for $SbCu_3$, $SnCu_4$, Cu_2Zn, Cu_3Al, whilst the lower forms do not show this property. And with salts, dimorphism is far more frequent with the anhydrous salts, and is only comparatively rarely observed among crystallohydrates. All these relations indicate that the fundamental typical compounds of the metals are those which correspond to the periodic system, while the lower forms, although more stable under ordinary conditions, must be regarded as the result of combinations of the fundamental form with an excess of metal, just as crystallohydrates are formed by the union of water with the anhydrous salt.'

[19b] The following short account of the alloys which have been most fully investigated up to the present day has the object of explaining in some measure what is said above concerning the alloys of copper. In this account I have availed myself of much that was communicated me by Mr. A. A. Baikoff.

The alloys of copper and tin, usually called bronzes, were first investigated by Rich, who recognised the formation of $SnCu_3$ and $SnCu_4$ among them. They were subsequently most intimate nature uniting physico-mechanical relations with the general laws of chemistry. 13. There is no doubt that many other

studied by many others with somewhat divergent results. Some (Le Chatelier and Herschkowitsch) admit only one compound, $SnCu_3$. This disparity is due to the fact that the fusing-point curves of the alloys have no maxima which would clearly indicate the composition of definite compounds, but show only 'critical' points. This is owing (Baikoff) to the facts: (1) that the compound $SnCu_4$ forms solid solutions with copper and (2) that the compound $SnCu_3$ decomposes in the act of fusion like salts containing water of crystallisation. The curve of fusion for the system $Cu + Sn$ was investigated with the greatest accuracy by Heycock and Neville. According to their data, there are two compounds, one having the composition $SnCu_4$ and containing exactly 32 per cent. of Sn and 68 per cent. of Cu, being indicated by a sharply defined bend in the curve for the alloy, the other, containing a larger proportion of tin, is also characterised by a 'critical' point, but its composition cannot be determined by the curve, as it decomposes in the act of fusion. This second compound is evidently $SnCu_3$, the existence of which is proved by the electrical conductivity (Matthiessen) and electro-motive force (Laurie, Herschkowitsch), and which was separated as a crystalline powder by Le Chatelier from alloys rich in tin by the action of hydrochloric acid. Rich also showed that $SnCu_3$ and $SnCu_4$ are the only alloys of copper and tin which do not liquate. Baikoff's observations on the fusing-points and micro-structure of these alloys showed that the alloy $SnCu_4$ solidifies completely at a constant temperature into a perfectly homogeneous alloy. All the alloys containing a greater proportion of tin and the alloy corresponding with the formula $SnCu_4$ show two pauses in solidifying, one break which is variable corresponding to the separation of crystals of $SnCu_4$, and the other, which is constant, to the transition of $SnCu_4$ into $SnCu_3$. This double fusing-point of $SnCu_3$ shows that this compound fuses with decomposition. The alloy $SnCu_4$ is dimorphous and passes from one crystalline form into another without in any way destroying the homogeneity of the alloy, although its structure is greatly modified by the changes. The dimorphism of the compound $SnCu_4$ explains the fact that bronze can be tempered. The alloy $SnCu_4$ is almost perfectly white, and is known as 'speculum metal,' as it is used for making mirrors and reflectors.

Alloys of copper and zinc are known as brasses. Researches on the fusing-points (Charpy), micro-structure (Charpy, Behrens, Le Chatelier), electro-motive force (Herschkowitsch), &c., indicate the existence of the compounds Cu_2Zn, $CuZn$, $CuZn_2$ (most easily recognised of all) and $CuZn_4$. The truth of such conclusions is further confirmed by the fact that there is a whole series of chemical analogies. Thus, according to Heycock and Neville, the system $Ag + Zn$ comprises compounds Ag_2Zn, $AgZn$, and $AgZn_2$; the system $Ag + Cd$: Ag_2Cd, and, according to Baikoff, the system $Cu + Cd$ includes compounds Cu_2Cd and $CuCd_2$. The alloys $Cu + Mg$ are found to give compounds Cu_2Mg and $CuMg$, but the compound $CuMg_2$ does not exist.

The alloys of copper and aluminium, according to the curve of fusion (Le Chatelier), comprise two compounds, $AlCu_3$ and Al_2Cu. The compound $AlCu_3$ corresponds to a maximum on the fusing-point curve, and may be separated from alloys rich in copper by the action of hydrochloric acid.

Copper and antimony, according to the researches of Baikoff, form two compounds, namely, $SbCu_3$ and $SbCu_2$. The former corresponds to a maximum on the curve of fusion; it is greenish-white, and fuses without decomposition at 680°. It exists in two dimorphous forms, the point of transition of which lies at about 410° C. $SbCu_3$ forms solid solutions with copper and antimony, and the property of tempering, which these alloys exhibit to as great an extent as steel, is due to the formation and splitting up of these solutions. The sp. grs. of the two polymorphic modifications of the compound $SbCu_3$ are different, namely, 8·51 with rapid cooling, and 8·68 when cooled slowly. The compound $SbCu_2$ fuses with decomposition at 586° C., and is characterised by a critical point on the fusion curve; it has a beautiful violet colour. The existence of these two compounds is also revealed by the hardness, electro-motive force, coefficient of expansion, and micro-structure of the alloys of Cu and Sb.

physical properties will, when further studied, also prove to be in periodic dependence on the atomic weights (see note 19), but at present only a few are known with any completeness, and we will only refer to the one which is the most easily and frequently determined—namely, the **specific gravity** in the solid and liquid states, the more especially as its connection with the chemical properties and relations of substances is shown at every step. Thus, for instance, of all the metals those of the alkalies, and of all the non-metals the halogens, are the most energetic in their reactions, and they have lower specific gravities than the neighbouring elements, as is seen in the accompanying tables, pp. 46 and 47. Such are sodium, potassium, rubidium, cæsium among the metals, and chlorine, bromine, and iodine among the non-metals; and as such less energetic metals as iridium, platinum, and gold (and even charcoal or the diamond) have higher specific gravities than the elements near to them in atomic weight, the degree of condensation of matter evidently influences the course of the transformations peculiar to a substance, and, furthermore, this dependence on the atomic weight, although very complex, is clearly of a periodic character. In order to account for this to some extent, it may be imagined that the lightest elements are porous, and, like a sponge, are easily penetrated by other substances, whilst the heavier elements are more compressed, and give way with difficulty to the insertion of other elements. These relations are best understood when, instead of the specific gravities referring to a unit of volume,[20] the **atomic volumes of the elements**—that is, the quotient A/d of the atomic weight A by the specific gravity d—are taken for comparison. As, according to the entire sense of the atomic theory, the actual matter of a substance does not fill up its whole cubical contents, but is surrounded by a medium (ethereal, as is generally imagined)—like the stars and planets which travel in the space of the heavens and fill it—with greater or less intervals, so the quotient A/d only expresses the *mean*

---

[20] Having occupied myself since the fifties (my dissertation for the degree of M.A. concerned the specific volumes, and is printed in part in the *Russian Mining Journal* for 1856) with the problems concerning the relations between the specific gravities and volumes and the chemical compositions of substances, I am inclined to think that the direct investigation of specific gravities gives essentially the same results as that of specific volumes, only that the latter are more graphic. Table III. of the periodic properties of the elements clearly illustrates this. Thus, for those members whose volume is the greatest among the contiguous elements, the specific gravity is least; that is, the periodic variation of both properties is equally evident. In passing, for instance, from silver to iodine we have a successive decrease of specific gravity and a successive increase of specific volume. The periodic alternation of the rise and fall of the specific gravity and specific volume of the free elements was communicated by me in August 1869 to the Moscow Meeting of Russian Naturalists. In the following year (1870) L. Meyer's paper appeared, which also dealt with the specific volumes of the elements.

volume corresponding to the sphere of the atoms, and therefore $\sqrt[3]{A/d}$ is **the mean distance between the centres of the atoms.** For compounds whose molecules weigh M, the mean magnitude of the atomic volume is obtained by dividing the mean molecular volume M/d by the number of atoms n in the molecule.[21] The above relations may easily be expressed from this point of view by comparing the atomic volumes. Those comparatively light elements which enter easily and frequently into reaction have the greatest atomic volumes: sodium 23, potassium 45, rubidium 57, cæsium 71, and the halogens about 27; whilst with those elements which enter into reaction with difficulty, the mean atomic volume is small; for carbon in the form of a diamond it is less than 4, and for charcoal about 6, for nickel and cobalt less than 7, for iridium and platinum about 9. The remaining elements having atomic weights and properties intermediate between those of the elements mentioned above have also intermediate atomic volumes. Therefore **the specific gravities and specific volumes of solids and liquids stand in periodic dependence on the atomic weights**, as is seen in the accompanying table, pp. 46 and 47, where both A (the atomic weight) and d (the specific gravity), and also A/d (specific volumes of the atoms) are given. Thus we find that in the large periods beginning with lithium, sodium, potassium, rubidium, cæsium, and ending with fluorine, chlorine, bromine, iodine, the extreme members (energetic elements) have a small density and large volume, whilst the intermediate substances gradually increase in density and decrease in volume—that is, as the atomic weight increases the density rises and falls, again rises and falls, and so on. Furthermore, the energy decreases as the density rises, and the greatest density is proper to the atomically heaviest and least energetic elements, for example, Os, Ir, Pt, Au, U.

In order to explain the relation between the volumes of the elements and of their compounds, the densities (column S) and volumes (column M/S) of some of the higher saline oxides arranged in the same order as in the case of the elements are given on pp. 46 and 47. For convenience of comparison the volumes of the oxides are all calculated per two atoms of an element combined with oxygen. For example, the density of $Al_2O_3=4{\cdot}0$; its weight, 102; and its volume, 25·5.

---

[21] In my opinion the mean volume of the atoms of compounds deserves more attention than has yet been paid to it. I may point out, for instance, that for feebly energetic oxides the mean volume of the atom is generally nearly 7, for example, for the oxides SiO_2, Sc_2O_3, TiO_2, V_2O_5, as well as ZnO, Ga_2O_3, GeO_2, ZrO_2, In_2O_3, SnO_2, Sb_2O_5, &c., whilst the mean volume of the atom of the alkali and acid oxides is greater than 7. Thus we find in the magnitudes of the mean volumes of the atom in oxides and salts both a periodic variation and a connection with their energy of essentially the same character as occurs in the case of the free elements.

Knowing the volume of aluminium to be 11, it is at once seen that in the formation of aluminium oxide, 22 volumes of it give 25·5 volumes of oxide, and therefore 3·5 volumes remain for O_3, or only 1·2 volume per atom of oxygen. A certain periodicity may also be observed with respect to the specific gravities and volumes of the higher saline oxides. But it is especially important to call attention to the fact that the volume of the alkali oxides is less than that of the metal contained in them, which is also expressed in the last column, giving this difference for each atom of oxygen.[22] Thus 2 atoms of sodium, or 46 volumes, give 24 volumes of Na_2O, and about 37 volumes of $2NaHO$; that is, the oxygen and hydrogen in distributing themselves in the medium of sodium have not only not increased the distance between its atoms, but have brought them nearer together, have drawn them together by the force of their great affinity, by reason, it may be presumed, of the small mutual attraction of the atoms of sodium. Such metals as aluminium and zinc, in combining with oxygen and forming oxides of feeble salt-forming capacity, hardly vary in volume; that is, only a small residue is left after subtracting the volume of the metal from that of the oxide; but the common metals and non-metals, and especially those forming acid oxides, always give an increased volume when oxidised; that is, the atoms are set further apart in order to make room for the oxygen. The oxygen in them does not compress the molecule as in the alkalies; it is therefore comparatively easily disengaged.

		M/S	Volume of Oxygen
H_2O	1·0	18	? — 22
Li_2O	2·0	15	— 9
Be_2O_2	3·06	16	+ 2·6
B_2O_3	1·8	39	+ 10·0
C_2O_4	1·6	55	+ 10·6
N_2O_5	1·64	66	? + 4
Na_2O	2·6	24	— 22
Mg_2O_2	3·5	23	— 4·5
Al_2O_3	4·0	26	+ 1·2
Si_2O_4	2·65	45	+ 5·2

[22] The volume of oxygen (judging by the table on this and the following pages) is evidently a variable quantity, forming a distinctly periodic function of the atomic weight and type of the oxide, and therefore the efforts which were formerly made to find the volume of the atom of oxygen in the volumes of its compounds may be considered to be futile. But since a distinct contraction always takes place in the formation of oxides, if the volume of an oxide is frequently less than the volume of the element combined with the oxygen, it might be surmised that the volume of oxygen in a free state is greater than its maximum calculated volume (11 for Ag_2O), and therefore about 12–15 (see note 24).

	S	M/S	Volume of Oxygen
P_2O_5	2·39	59	+ 6·2
S_2O_6	1·96	82	+ 8·7
Cl_2O_7	? 1·92	95	+ 6
K_2O	2·7	35	− 35
Ca_2O_2	3·25	34	− 8
Sc_2O_3	3·86	35	? 0
Ti_2O_4	4·2	38	+ 3
V_2O_5	3·49	52	+ 6·7
Cr_2O_6	2·74	73	+ 9·5
Cu_2O	5·9	24	+ 9·6
Zn_2O_2	5·7	23	+ 4·8
Ga_2O_3	? 5·1	36	+ 4
Ge_2O_4	4·7	44	+ 4·5
As_2O_5	4·1	56	+ 6·0
Sr_2O_2	4·7	44	− 13
Y_2O_3	5·0	45	? − 2
Zr_2O_4	5·5	44	0
Nb_2O_5	4·7	57	+ 6
Mo_2O_6	4·4	65	+ 6·8
Ag_2O	7·5	31	+ 11
Cd_2O_2	8·0	32	+ 3
In_2O_3	7·18	38	+ 2·7
Sn_2O_4	7·0	43	+ 2·7
Sb_2O_5	6·5	49	+ 2·6
Te_2O_6	5·1	68	+ 4·7
Ba_2O_2	5·7	52	− 10
La_2O_3	6·5	50	+ 1
Ce_2O_4	6·74	50	+ 2
Ta_2O_5	7·5	59	+ 4·6
W_2O_6	6·8	68	+ 8·2
Hg_2O_2	11·1	39	+ 4·5
Pb_2O_4	8·9	53	+ 4·2
Th_2O_4	9·86	54	+ 2

As the volumes of the chlorides, the organo-metallic and all other corresponding compounds also vary in a like periodic succession with a change of elements, it is evidently possible to indicate the properties of substances yet uninvestigated by experimental means, and even those of yet undiscovered elements. It was possible by following this method to foretell, on the basis of the periodic law, many of the properties of scandium, gallium, and germanium, which were verified with great accuracy after these metals had been discovered.[23] The periodic law, therefore, has not only embraced the mutual relations of the elements and expressed their analogy, but has also to a certain extent subjected to law the doctrine of the types of the compounds formed by the elements: it has enabled us to see a regularity in the variation of all chemical and physical properties of elements and compounds,[24] and

---

[23] As an example we will take indium oxide, In_2O_3. Its sp. gr. and sp. vol. should be the mean of those of cadmium oxide, Cd_2O_2, and stannic oxide, Sn_2O_4, as indium stands between cadmium and tin. Thus in the seventies it was already evident that the volume of indium oxide should be about 38, and its sp. gr. about 7·2, which was confirmed by the determinations of Nilson and Pettersson (7·179) made in 1880.

[24] As the distance between, and the volumes of, the molecules and atoms of solids and liquids certainly enter into the data for the solution of the problems of molecular mechanics, which as yet have only been worked out to any extent for the gaseous state, the study of the specific gravity of solids, and especially of liquids, has long had an extensive literature. With respect to solids, however, a great difficulty is met with, owing to the specific gravity varying not only with a change of isomeric state (for example, for silica in the form of quartz it is 2·65, and in that of tridymite, 2·2), but also directly under mechanical pressure (for example, in a crystalline, cast, and forged metal), and even with the extent to which they are powdered, &c., which influences are imperceptible in liquids (compare Chap. XIV., note 55a).

Without going into further details, we may add to what has been said above that the conception of specific volumes and atomic distances has formed the subject of a large number of researches, but as yet it is only possible to lay down a few generalisations given by Dumas, Kopp, and others, which are mentioned and amplified by me in my work cited in note 20, and in my memoirs on this subject.

1. Analogous compounds and their isomorphs have frequently approximately the same molecular volumes.

2. Other compounds, analogous in their properties, exhibit molecular volumes which increase with the molecular weight.

3. When a contraction takes place in combination in a gaseous state, then, in the majority of instances, contraction is also to be observed in the solid or liquid state; that is, the sum of the volumes of the reacting substances is greater than the volume of the resultant substance or substances.

4. In decomposition the reverse of that which occurs in combination takes place.

5. In substitution (when the volumes in a state of vapour do not vary) a very small change of volume generally takes place; that is, the sum of the volumes of the reacting substances is almost equal to the sum for the resultant substances.

6 Hence it is impossible tc judge of the volumes of the component substances from that of a compound, although it is possible to do so from the product of substitution.

7. The replacement of H_2 by sodium, Na_2, and by barium, Ba, as well as the replacement of SO_4 by Cl_2, scarcely changes the volume; but the volume increases with the replacement of Na by K, and decreases with the replacement of H_2 by Li_2, Cu, and Mg.

8. There is no need for comparing volumes in a solid and a liquid state at the so-called corresponding temperatures; that is, at temperatures at which the vapour pressure is the same in each case. The comparison of volumes at the ordinary temperature is sufficient for finding a regularity in the relations of volumes (this deduction was developed by me in particular detail in 1856).

has rendered it possible to foretell the properties of elements and compounds yet uninvestigated by experimental means; thus it has prepared the ground for the building up of atomic and molecular mechanics.[25]

---

9. Many investigators (Perseau, Schröder, Löwig, Playfair and Joule, Baudrimont, Einhardt) have sought in vain for a multiple proportion in the specific volumes of solids and liquids.

10. The truth of the above is seen very clearly in comparing the volumes of polymeric substances. The volumes of their molecules are equal in a state of vapour, but are very different in a solid and a liquid state, as is seen from the close resemblance of the specific gravities of polymeric substances. But as a rule the more complex polymerides are denser than the simpler.

11. We know that the hydroxides of light metals have generally a smaller volume than the metals, whilst that of magnesium hydroxide is considerably greater, which is explained by the stability of the former and the instability of the latter. In proof of this we may cite, besides the volumes of the true alkali metals, the volume of barium (36) which is greater than that of its stable hydroxide (sp. gr. 4·5, sp. vol. 30). The volumes of the salts of magnesium and calcium are greater than the volume of the metal, with the single exception of the fluoride of calcium. With the heavy metals the volume of the compound is always greater than the volume of the metal, and, moreover, for such compounds as silver iodide, AgI (d = 5·7), and mercuric iodide, HgI_2 (d = 6·2, and its volume, 73), the volume of the compound is greater than the sum of the volumes of the component elements. Thus the sum of the volumes Ag + I = 36, and the volume of AgI is 41. This stands out with particular clearness on comparing the volumes K + I = 71 with the volume of KI, which is equal to 54, its density being 3·06.

12. In such combinations, between solids and liquids, as solutions, alloys, isomorphous mixtures, and similar feeble chemical compounds, the sum of the volumes of the reacting substances is always very nearly that of the resulting substance, but here the volume is either slightly larger or smaller than the original; speaking generally, the amount of contraction depends on the force of affinity acting between the combining substances. I may here observe that the present data respecting the specific volumes of solid and liquid bodies deserve a fresh and full elaboration to explain many contradictory statements which have accumulated on this subject. As regards liquefied gases at their melting-points, I think it well to cite the following table given by Dewar (1900):—

Liquid	Sp. gr. at melting-point	Sp. vol.
Hydrogen	0·086	11·7
Nitrogen	1·10	13·1
Oxygen	1·27	12·6

The volume is naturally greater at the corresponding boiling-points, and at the absolute zero (−273°) the specific volumes approach 10–12; that is to say, they become almost equal.

[25] In demonstrating those aspects of the periodic law which speak most clearly in its favour, I consider it futile to discuss the numerous attacks which have been made on it, because they either throw no new light upon the law, or else have been refuted by further research. On the other hand I consider it necessary to mention three points concerning the periodic law which have not yet been reconciled with it, namely: (1) the atomic weights of cobalt and nickel, (2) the atomic weight of tellurium, and (3) the position of the so-called rare metals.

(1) Notwithstanding repeated and recent determinations of the atomic weights of Co and Ni, it is always found that, although these are very nearly equal, yet the atomic weight of Co is slightly larger than that of Ni, the value for Co being about 59·0 and that for Ni, 58·7; while, according to their analogy, and therefore according to the periodic

system, the atomic weight of Ni should be greater than that of Co, for they both stand between Fe = 55·9 and Cu = 63·6, and nickel approaches in all respects more nearly to Cu than to Fe, and Co more closely resembles Fe than Cu in its properties.

What is most wanted here are more new discriminative and *comparative* researches of great exactitude (such as the analysis of similar corresponding compounds of Ni and Co), for the results of different investigators cannot be said to be in perfect accord, and C. Winkler's researches even give the atomic weight of Ni as 59·4, which cannot, however, be the case. Moreover, nickel may be purified from the metals accompanying it in the form of a volatile compound $Ni(CO)_4$, more perfectly than cobalt, and neither nickel nor cobalt offers such properties in its analogous compounds (oxides and salts) as could absolutely guarantee their being of strictly definite and constant composition. In a word there are many practical difficulties, and no chemist would, I think, deny that new researches might alter those decimals of the atomic weights which are in question. But even if the atomic weight of Ni eventually proves to be undoubtedly greater than Co, this would in no wise disturb the essence of the periodic law, especially as the question concerns the most uncertain group VIII., where the higher saline oxides are variable in composition and have no very distinctly marked properties. It is my personal opinion, however, that the atomic weight of Co most requires re-determining, and that it will prove less than that now accepted (Co = 59·0) and less than that of Ni.

(2) Tellurium, in forming a higher saline oxide, TeO_3, should certainly belong to group VI., and iodine, I, which gives HIO_4 and I_2O_7, to group VII.; and yet Stas determined the generally adopted atomic weight I = 126·85, and many recent determinations give Te = about 127·1, which is greater than that of iodine, although Brauner and others have frequently found the atomic weight of Te to be less than that of I. My own opinion has long been (since 1898, see vol. xxiii., *Encyclopædic Dictionary*, 'Periodic Law') that iodine should have an atomic weight greater than 126·85 and probably greater than 127, as mentioned in Chap. XI., note 62. In Ladenburg's recent (1902) determinations the iodine was dried over $CaCl_2$, and it probably contained some chlorine (see also Chap. XX.).

(3) Among the so-called rare metals (Chap. XVII.) yttrium and cerium, the representatives of two special groups, found their position in the periodic system soon after the law was confirmed, and I determined the atomic weight of yttrium and also the specific heat of cerium with the object of seeing if the proposed modifications of their atomic weights (for yttrium from YO to Y_2O_3, and for cerium from Ce_3O_4 to CeO_2) were permissible. All the subsequent researches of many chemists, and especially of Brauner, have confirmed the justice of my proposal, and the result has been extended not only to La and Di (this was done by me), but also to all the other rare metals whose oxides have since then been given the composition R_2O_3, and scandium was found by Nilson to correspond to the looked-for ekaboron, Sc = 44·1. The number of metals of this class subsequently became greater, and now those enumerated in Chap. XVII. are more or less known. A common composition, R_2O_3, is given to the oxides (basic) of all these metals, on the strength of their analogy with the oxides R_2O_3 of yttrium, cerium, &c., which have found their proper position in the periodic system. There is no place in group III. of the periodic system for some of the rare metals with the type of oxide R_2O_3, although there are two series of unoccupied places for elements with atomic weights 140–183, between Ce = 140 and Ta = 183. I have not formed any precise opinion on this score, and this appears to me to be one of the most difficult problems offered to the periodic law. However, the investigation of many of these metals is evidently insufficient to form a true opinion respecting the composition of their oxides, and in some cases even to be sure of their being independent elements, and I therefore think it premature to form a definite decision. At the Congress of Russian Naturalists in 1901, Prof. Brauner proposed placing all the rare metals about Ce, counting their atomic weights 140–183, in a special auxiliary group. I am not able to refute such a conclusion, but I think, however, that it would be more prudent to leave this question open, all the more so since Yb = 173 (one of the best investigated of the rare metals) corresponds quite well, according to its atomic weight, to the position III., 10.

The higher hydrogen and organo-metallic compounds R=H, CH_3,...	The elements and their atomic weights.	The higher saline compounds $X=\frac{1}{2}O$, (OH), Cl, (NO_3), (OM), where $M=K, \frac{1}{2}Ca, \frac{1}{3}Al$, &c.	Simple bodies (elements).						
			Composition of the molecule.	Sp. gr. in solid and liquid states.		Sp. vol. in solid and liquid states.		Melting-point.	
RH	H = 1·008		H_2	0·08	max.	12		−256°	
	He = 4·0		He						
RLi	Li = 7·03	LiX	Li	0·59	max.	12		+185°	
R_2Be	Be = 9·1	BeX_2	Be ?	1·64		5·5		+950°	
R_3B	B = 11·0	BX_3	B_n	2·5		4·4	min.	+1300° ?	
R_4C	C = 12·0	CX_4	C_n	1·9		6·3		+2700° ?	
R_3N	N = 14·04	NX . . . NX_5	N_2	1·1		13		215°	
R_2O	O = 16·000	OX_2	O_2	1·27		12	min.	−250°	
RF	F = 19·0	FX	F_2	1·14	max.	17		−210°	
	Ne = 19·9		Ne					−250° ?	
RNa	Na = 23·05	NaX	Na	0·98	max.	24		+97°	
R_2Mg	Mg = 24·3	MgX_2	Mg	1·74		14		700°	
R_3Al	Al = 27·0	AlX_3	Al	2·6		11	min.	657°	
R_4Si	Si = 28·4	SiX_4	Si_n	2·5		11	min.	max. 1300° ?	
R_3P	P = 31·0	PX_5	P_4	2·2		14		+44°	
R_2S	S = 32·06	SX_6	S_6	2·07		15		+114°	
RCl	Cl = 35·45	ClX . . . . ClX_7	Cl_2	1·3	max.	27		−100°	
	Ar = 38 ?		Ar					−190°	min.
	K = 39·1	KX	K	0·87	max.	45		+60°	
	Ca = 40·1	CaX_2	Ca ?	1·56		26		+800°	
	Sc = 44·1	ScX_3	Sc ?	2·5?		18 ?		1200° ?	
	Ti = 48·1	TiX_4	Ti ?	3·6		13		2000° ?	
	V = 51·4	VX_5	V ?	5·5		9		max. 2500° ?	
	Cr = 52·1	CrX_6	Cr ?	6·7		7·7		1850° ?	
	Mn = 55·0	MnX_2 . . . MnX_7	Mn	7·5		7·3		1500°	
	Fe = 55·9	FeX_6	Fe	7·8		7·2		1450°	
	Co = 59 ?	CoX_4	Co	8·6		6·8		1400°	
	Ni = 59 ?	NiX_3	Ni	8·7		6·8	min.	1350°	
RCu	Cu = 63·6	CuX, CuX_2	Cu	8·8		7·2		1054°	
R_2Zn	Zn = 65·4	ZnX_2	Zn	7·1		9·2		419°	
R_3Ga	Ga = 70·0	GaX_3	Ga ?	5·96		11·7		30°	min.
R_4Ge . . .	Ge = 72·3	GeX_4	Ge	5·47		13·2		max. 900°	
R_3As	As = 75·0	AsX_5	As_4	5·65		13·3		500°	
R_2Se	Se = 79 ?	SeX_6	Se_6 ?	4·8		16		+217°	
RBr	Br = 79·95	BrX . . . . BrX_7	Br_2	3·1	max.	26		−7	
	Kr = 81·8		Kr					−100° ?	min
	Rb = 85·4	RX	Rb	1·5	max.	57		+39°	
	Sr = 87·6	SrX_2	Sr	2·5		35		600° ?	
	Y = 89·0	YX_3	Y?	3·4		26		1000° ?	
	Zr = 90·6	ZrX_4	Zr_n ?	4·1		22		1500° ?	
	Nb = 94	NbX_5	Nb ?	7·1		13		1700° ?	
	Mo = 96	MoX_6	Mo ?	8·6		11		max. 2200° ?	
	? = 99 ?	unknown ekamanganese.							
	Ru = 101·7	RuX_2 . . . RuX_8	Ru	12·2		8·3	min.	2000° ?	
	Rh = 103·0	RhX_6	Rh	12·1		8·5		2000° ?	
	Pd = 106·5	PdX_4	Pd	11·8		9·0		1800°	
	Ag = 107·9	AgX	Ag	10·5		10·3		950°	
R_2Cd	Cd = 112·4	CdX_2	Cd	8·6		13		320°	
R_3In	In = 114·0	InX_3	In	7·4		14		176°	min.
R_4Sn	Sn = 119·0	SnX_4	Sn	7·2		16		232°	
R_3Sb	Sb = 120	SbX_5	Sb ?	6·7		18		432°	
R_2Te	Te = 127 ?	TeX_6	Te ?	6·4		20		455°	
RI	I = 127 ?	IX . . . . . IX_7	I_2	4·9		26		115°	

The higher hydrogen and organo-metallic compounds $R=H, CH_3$...	The elements and their atomic weights.	The highest saline compounds $X=\frac{1}{2}O$, (OH), Cl, (NO_3), (OM), where $M=K, \frac{1}{2}Ca, \frac{1}{3}Al$, &c.	Simple bodies (elements).			
			Composition of the molecule.	Sp. gr. in solid and liquid states.	Sp. vol. in solid and liquid states.	Melting-point.
	Xe = 128					
	Cs = 132·9	CsX	Cs ?	2·4	max. 56	27° min.
	Ba = 137·4	BaX_2	Ba ?	3·8	36	?
	La = 139	LaX_3	La ?	6·1	23	?
	Ce = 140	CeX_4	Ce	6·6	21	700° ?
	There is an unknown whole large period from Ce = 140 to Ta = 183. If the oxides be taken as R_2O_3, this period includes the rare metals Pr = 140, Nd = 144, Sm = 150?, Gd = 156, Tb = 160, Er = 166, Tu = 171, and Yb = 173.					
	Ta = 183	TaX_5	Ta ?	10·4	18	?
	W = 184	WX_6	W ?	19·1	9·6	2600°
	Unknown element: dimanganese? 188?					
	Os = 191	OsX_3 . . . OsX_8	Os ?	22·5	min. 8·5	max. 2700°
	Ir = 193	IrX_6	Ir	22·4	8·6	2000°
	Pt = 194·9	PtX_4	Pt	21·4	9·2	1775°
	Au = 197·2	AuX . AuX_3	Au	19·3	10	+1045°
R_2Hg	Hg = 200·0	HgX_2	Hg	13·6	15	−39° min.
R_3Tl	Tl = 204·1	TlX_3	Tl	11·8	17	+294°
R_4Pb	Pb = 206·9	PbX_4	Pb	11·3	18	328°
R_3Bi	Bi = 208	BiX_3 . . BiX_5	Bi	9·8	21	269°
	Unknown elements with atomic weights from 208 to 232. Probably radium, Rd = 224, discovered by Madame Curie, belongs to this series.					
	Th = 232	ThX_4	Th ?	11·1	21	1700° ?
	U = 239	UX_6	U ?	18·7	13	

CHAPTER XVI

ZINC, CADMIUM, AND MERCURY

THESE three metals, like magnesium, give oxides RO, which form feebly energetic bases, and are also volatile. The volatility increases with the atomic weight. Magnesium can be distilled at a white heat, zinc at a temperature of about 930°, cadmium at about 770°, and mercury at about 357°. Their oxides, RO, are more easily reducible than magnesia, that of mercury being the most easily reducible. The properties of their salts RX_2 (solubility, power of forming double and basic salts, and many other qualities) are in many respects identical with those of MgX_2. The difficulty with which they are oxidised, the instability of their compounds, the density of the metals and their compounds, their scarcity in nature, and many other properties increase gradually with the atomic weight. Their characteristics, as contrasted with those of magnesium, are to be expected from the fact that zinc, cadmium, and mercury are heavy metals.

Zinc stands nearest to magnesium in atomic weight and in many properties. Thus, for instance, zinc sulphate, or white vitriol, easily crystallises with seven molecules of water, $ZnSO_4,7H_2O$. It is isomorphous with Epsom salts, and parts with difficulty with the last molecule of water; it forms double salts—for instance, $ZnK_2(SO_4)_2,6H_2O$ —exactly as magnesium sulphate does.[1] **Zinc oxide**, ZnO, is a white powder, almost insoluble in water,[2] like magnesia, from which, how-

---

[1] Zinc sulphate is often obtained as a by-product—for instance, in the action of galvanic batteries containing zinc and sulphuric acid. When the anhydrous salt is heated it forms zinc oxide, sulphurous anhydride, and oxygen. The solubility in 100 parts of water at 0° is 43; at 20°, 53; at 40°, 63½; at 60°, 74; at 80°, 84½; and at 100°, 95 parts of anhydrous zinc sulphate—so that it is closely expressed by the formula, $43 + 0{\cdot}52t$.

An admixture of iron is often found in ordinary sulphate of zinc in the form of ferrous sulphate, $FeSO_4$, isomorphous with the zinc sulphate. In order to separate this, chlorine is passed through the solution of the impure salt (when the ferrous salt is converted into ferric), the solution is then boiled and zinc oxide afterwards added, which, after some time has elapsed, precipitates all the ferric oxides. Ferric oxide, of the form R_2O_3, is displaced by zinc oxide, of the form RO.

[2] Zinc oxide (flores zinci) is obtained by the combustion and oxidation of zinc, and by the ignition of some of its salts; for instance, those of carbonic and nitric acids; it is likewise precipitated by alkalies from a solution of ZnX_2 in the form of a gelatinous

ever, it is distinguished by its solubility in solutions of sodium and potassium hydroxides.[3] Zinc chloride[4] is decomposed by water,

---

hydroxide. The oxide produced by roasting zinc blende, ZnS (burning in the air, when the sulphur is converted into sulphurous anhydride), contains various impurities. For purification, the oxide is mixed with water, and the sulphurous anhydride formed by roasting the blende is passed through it. Zinc bisulphite, $ZnSO_3,H_2SO_3$, then passes into solution. If a solution of this salt be evaporated, and the residue ignited, zinc oxide, free from many of its impurities, will remain. Zinc oxide is a light white powder, used as a paint instead of **white lead**; the basic salt, corresponding with magnesia alba, is used for the same purpose, as also is a mixture of ZnS and $BaSO_4$, called lithophone. V. Kouriloff (1890), by boiling the hydrate of the oxide with a 3 per cent. solution of peroxide of hydrogen, obtained $Zn_2H_2O_4$ or the hydrate of the peroxide ($=ZnO_2,ZnH_2O_2$ or a compound of 2ZnO with H_2O_2), which did not part with its oxygen at 100°, but only above 120°. Cadmium gives a similar compound of a yellow colour. Magnesium, although it forms such a compound, only does so with great difficulty.

[3] For the solution of one part of the oxide 55,400 parts of water are required. Nevertheless, even in such a weak solution, zinc oxide (hydroxide, ZnH_2O_2) changes the colour of red litmus paper like a base. Zinc oxide is obtained in the wet way by adding an alkali hydroxide to a solution of a zinc salt; for instance: $ZnSO_4 + 2HKO = K_2SO_4 + ZnH_2O_2$. The gelatinous precipitate of zinc hydroxide is **soluble** in an excess of **alkali** which clearly distinguishes it from magnesia. This solubility of zinc hydroxide in alkalies is due to the power of zinc oxide to form a compound, although an unstable one, with alkalies—that is to say, it points to the fact that zinc oxide already belongs partly to the intermediate oxides. The oxides of the metals above mentioned (except BeO) do not show this property. The property which metallic zinc itself has of dissolving in caustic alkali with the disengagement of hydrogen (the solution is facilitated by contact with platinum or iron) depends on the formation of such a compound of the oxides of zinc and the alkali metals. The solution of zinc hydroxide, ZnH_2O_2, in potash (in a strong solution), proceeds when these hydrates are taken in the proportion, $ZnH_2O_2 + KHO$. If such a solution is evaporated to dryness, water extracts only caustic potash from the fused residue. When a solution of zinc hydroxide in strong alkali is mixed with a large mass of water, nearly all the oxide of zinc is precipitated; and, therefore, in weak solutions, a large quantity of the alkali is required to effect solution, which points to the decomposition of the zinc-alkali compounds by water (Kouriloff, Rubenbauer, and others). If strong alcohol is added to a solution of zinc oxide in sodium hydroxide, the crystallohydrate, $2Zn(OH) ONa),7H_2O$, separates. Strong solutions of caustic soda dissolve zinc hydroxide when the two are in the proportion, $Zn(HO)_2 : 2NaOH$, that is, when $ZnNa_2O_2$ is formed; but the solution decomposes spontaneously with the formation of a precipitate, and leaves a solution in which the amount of zinc varies with the concentration, the greatest amount being left when about 3NaHO are taken to $Zn(OH)_2$ and when there is about half a litre of water to a gram-molecular weight of NaHO. Here, as in other similar instances, the hydroxide undergoes a colloidal transformation.

[4] **Zinc chloride**, $ZnCl_2$, is generally employed in the arts in the form of a solution obtained by dissolving zinc in hydrochloric acid. This solution is used for soldering metals, impregnating railway sleepers, &c. The reason why it is thus employed may be understood from its properties. When evaporated it first parts with its water of crystallisation; on being further heated, however, it loses all traces of water, and forms an oily mass of anhydrous salt which solidifies on cooling. This substance melts at 250°, commences to volatilise at about 400°, and boils at 730°. The soldering of metals—that is, the introduction of an easily fusible metal between two contiguous metallic objects—is hindered by any film of oxide upon them; and, as heated metals easily oxidise, they are naturally difficult to solder. Zinc chloride is used to prevent the oxidation. It fuses on being heated, and, covering the metal with an oily coating, prevents contact with the air; but even if any oxide has formed, the free hydrochloric acid generally existing in the zinc chloride solution dissolves it, and in this way the metallic surface of the metals

combines with ammonium chloride, potassium chloride, &c., just like magnesium chloride, forms an oxychloride, and also combines with zinc oxide.[4a]

---

to be soldered is preserved fit for the adhesion of the liquid solder, which on cooling binds the objects together. Much zinc chloride is used also for steeping wood (telegraph posts and railway sleepers) in order to preserve it from decaying quickly. This preservative action is in all probability mainly due to the poisonous character of zinc salts (corrosive sublimate is even more poisonous, and a still better agent to preserve wood from decay), since decay is due to the action of lower organisms. The same object is attained by creosote, phenol, and other substances which hinder the growth of the lower organisms.

The specific gravities of solutions containing p per cent. of zinc chloride, $ZnCl_2$, are as follows:—

p =	10	20	30	40	50
15°/4° =	1·093	1·184	1·293	1·411	1·554
ds/dt =	−3	−5	−7	−8	−9

The last line shows the change of specific gravity for 1° in ten-thousandth parts for temperatures near 15°. More accurate determinations of Cheltzoff, personally communicated by him, led him to conclude that solutions of zinc chloride follow the same laws as solutions of sulphuric acid, which will be considered in Chap. XX.: (1) from H_2O to $ZnCl_2,120H_2O$, $s = S_0 + 92{\cdot}85p + 0{\cdot}1748p^2$ (2) thence to $ZnCl_2,40H_2O$, $s = S_0 + 93{\cdot}96p - 0{\cdot}0126p^2$; (3) thence to $ZnCl_2,25H_2O$, $s = 11481{\cdot}5 + 96{\cdot}45\ (p - 15{\cdot}89) + 0{\cdot}4567\ (p - 15{\cdot}89)^2$; (4) thence to $ZnCl_2,10H_2O$, $s = 12212{\cdot}1 + 104{\cdot}82\ (p - 23{\cdot}21) + 0{\cdot}7992\ (p - 23{\cdot}21)^2$; (5) thence to $p = 65$ per cent., $s = 14606{\cdot}3 + 140{\cdot}96\ (p - 43{\cdot}05) + 1{\cdot}4905\ (p - 43{\cdot}05)^2$, where s is the specific gravity of the solution at 15°, containing p per cent. of $ZnCl_2$ by weight, taking water at $4° = 10000$, and where $S_0 = 9991{\cdot}6$ (specific gravity of water at 15°).

Zinc chloride has a great affinity for water; it is not only soluble in it, but also in alcohol, and on being dissolved in water becomes considerably heated, like magnesium and calcium chlorides. Zinc chloride is capable of taking up water, not only in a free state, but also in chemical combination with many substances, and therefore it is used in organic researches for removing the elements of water from many of the organic compounds.

[4a] When mixed with zinc oxide it forms, with remarkable ease, a very hard mass of **zinc oxychloride**, which is applied in the arts—for instance, in painting—to resist the action of water or for cementing such objects as are destined to remain in water. Zinc oxychloride, $ZnCl_2,3ZnO,2H_2O (= Zn_2OCl_2,2ZnH_2O_2)$, is also formed from a solution of zinc chloride by the action of a small quantity of ammonia on it after heating the precipitate obtained for a considerable time with the liquid; the admixture of ammonium salts with a mixture of a strong solution of zinc chloride with its oxide makes a similar mass, which does not solidify so rapidly, and is therefore more useful in some cases. Moisture and cold do not change the hardened mass of oxychloride, which also resists the action of many acids and a temperature of 300°, and is hence a useful cement for many purposes. (A solution of magnesium chloride with magnesium oxide forms a similar oxychloride.) The mass solidifies best when there are equal quantities by weight of zinc in the chloride and oxide, and therefore when it has the composition Zn_2OCl_2. In preparing such a cement, naturally zinc oxide alone may be taken, and the requisite quantity of hydrochloric acid added to it.

The capacity of $ZnCl_2$ to combine with water, ZnO, and HCl (and also with other metallic chlorides) indicates its property to combine with molecules of other substances, and therefore its compounds with NH_3, and especially a compound, $ZnCl_2,2NH_3$, similar to sal-ammoniac, might be expected (i.e., $2NH_4Cl$, in which H_2 is replaced by Zn). And indeed it has long been known that $ZnCl_2$ absorbs ammonia and gives solid substances capable of dissociating with the disengagement of NH_3. Among these compounds

Zinc, like many heavy metals, is often **found in nature in combination with sulphur**, forming the so-called **zinc blende,**[5] ZnS. This sometimes occurs in large masses, often crystallised in cubes; it is frequently translucent, and has a metallic lustre, although this is not so clearly developed as in many other metallic sulphides with which we shall hereafter become acquainted. The ores of zinc also comprise the **carbonate and silicate, a mixture of which is known as calamine.**

Metallic zinc (spelter) is most frequently obtained from the ores containing the carbonate[6]—that is, from calamine, which is sometimes found in thick veins, for instance, in Poland, in Galicia, on the banks of the Rhine, and in considerable masses in Belgium and England. In Russia beds of zinc ore are met with in Poland and the Caucasus, but the output is small. In Sweden, as early as the fifteenth century, calamine was worked up into an alloy of zinc and copper (brass), and Paracelsus produced zinc from calamine; but the technical production of the metal itself, long ago practised in China, only commenced in Europe in 1807—in Belgium, when the Abbé Donnet discovered that zinc was volatile. From that time the production has increased to about 400,000 tons annually.

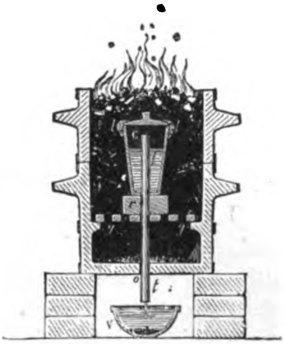


FIG. 90.—Distillation of zinc in a crucible placed in a furnace. *o c*, tube along which the vapour passes and condenses.

The reduction of metallic zinc from its ores is based on the fact

---

Isambert and V. Kouriloff (1894) obtained $ZnCl_2,6NH_3$, $ZnCl_2,4NH_3$, $ZnCl_2,2NH_3$, and $ZnCl_2,NH_3$. The dissociation pressures of the two last-mentioned compounds at 218° are equal to 43·6 mm. and 6·7 mm. respectively. $CdCl_2$ also forms similar compounds with NH_3 (Kouriloff, 1894).

[5] This mineral has been given the name of 'mock-ore,' on account of its having the appearance (considerable density, 4·06, &c.) of ordinary metallic ores; it deceived the first miners, because it did not, like other ores, give metal when simply roasted in air and fused with charcoal. The white zinc oxide, formed by burning the vapours of zinc, was also called 'nihil album,' or 'white nothing,' on account of its lightness.

[6] It may here be mentioned that by the word **ore** is meant a hard, heavy substance, which is dug out of the earth and used in metallurgical works for obtaining the ordinary heavy metals long known and used. The natural compounds of sodium or magnesium are not called ores, because magnesium and sodium have not been long obtainable in quantity. The heavy metals, which are easily reduced and do not easily oxidise, are those which are exclusively directly applied in manufactures. Ores either contain the metals themselves (for instance, ores of silver or bismuth), and the metals are then said to be in a native state, or else their sulphur compounds (blende, mock-ore, pyrites—as, for example, galena, PbS; zinc blende, ZnS; copper pyrites, CuFeS) or oxides (as the ores of iron), or salts (calamine, for instance). Zinc is incomparably rarer than magnesium, and is only well known because it is transformed from its ores into a metal which finds direct use in many branches of industry.

that zinc oxide[7] is easily reduced by charcoal at a red heat: $ZnO + C = Zn + CO$. The zinc thus obtained is in a finely divided state and impure, being mixed with other metals reduced with it, but the greater portion is **converted into vapour**, from which it easily passes into a liquid or solid state. The reduction and distillation are carried on in earthenware retorts, filled with a mixture of the divided ore and charcoal. The vapours of zinc and gases formed during the reaction escape by means of a pipe leading downwards, and are led to a chamber where the vapours are cooled. By this means they do not come into contact with the air, because the neck of the retort is filled with gaseous carbonic oxide, and therefore the zinc does not oxidise; otherwise its vapour would burn in the air.[7a] The vapours of zinc, entering the cooling chamber, condense into white zinc powder or zinc dust. When the neck of the retort is heated the zinc is obtained in a liquid state, and is cast into plates, in which form it is generally sold.

Commercial zinc is generally impure, containing lead, arsenic, particles of carbon, iron, and other metals carried over with the vapours, although they are not volatile at a temperature approaching 1000°, at which zinc is volatilised. If it be required to obtain pure zinc from the commercial article, the latter is subjected to a further slow distillation in a crucible with a pipe passing through the bottom, the vapours formed by the heated zinc only having exit through the pipe cemented into the bottom of the crucible, if the covers are properly luted on. Passing through this pipe, the vapours condense to a liquid, which is collected in a receiver. Zinc thus purified is generally re-melted and cast into rods, and in this form is often used for physical and chemical researches where a pure article is required.[8]

---

[7] After being extracted from the earth by the miners, ores are often enriched by sorting, washing, and other mechanical operations. The sulphurous ores (and likewise others) are then generally roasted. Roasting an ore means heating it to redness in air. The sulphur then burns, and passes off in the form of sulphurous anhydride, SO_2, and the metal oxidises. The roasting is carried on in order to obtain an oxide instead of a sulphur compound, the oxide being reducible by charcoal. These methods, introduced ages ago, are met with in nearly all metallurgical works for practically all ores. For this reason the preparatory treatment of zinc blende furnishes zinc oxide: this is already contained in calamine.

[7a] With very impure ores, especially such as contain lead (PbS often accompanies zinc), the vapour of the reduced zinc is allowed to pass directly into the air. It burns and gives ZnO, which is used as a pigment. A considerable amount of zinc is now obtained by electrolysis, by the action of an electric current on solutions of chloride of zinc, which is obtained as a by-product from the ores of other metals in separating the zinc they contain by hydrochloric acid. The zinc obtained by electrolysis is generally purer than that prepared by volatilisation. Further details will be found in works on electro-metallurgy.

[8] This zinc, although homogeneous, still contains certain impurities, to remove which

Metallic zinc has a bluish-white colour; its lustre, compared with that of many other metals, is insignificant. When cast it exhibits a crystalline structure. Its specific gravity is about 7, varying from 6·8 to 7·2, according to the degree of compression (by forging, rolling, &c.) to which it has been subjected. It is very ductile, considering its hardness. For this reason it chokes up files when being worked. Its malleability is considerable when pure, but in the ordinary impure condition in which it is sold, it is impossible to roll it at the ordinary temperature, as it easily breaks. At a temperature of 100°, however, it easily undergoes such operations, and can then be drawn into wire or rolled into sheets. If heated further it again becomes brittle, and at 200° may be even crushed into powder, so completely does it lose its molecular cohesion. It melts at 418°, and distils at 930°.

Zinc does not undergo any change in the atmosphere. Even in very damp air it only becomes coated with a thin white coating of oxide. For this reason it is available for all objects which are only in contact with air. Sheet zinc may therefore be used for roofing and many other purposes.[9] This great stability of zinc in air shows its slight energy with regard to oxygen as compared with the metals already mentioned, which are capable of reducing zinc from solutions. But zinc plays this part with regard to the remaining metals; for example, it reduces salts of lead, copper, mercury, &c. Although zinc is an almost unoxidisable metal at the ordinary temperature, it burns in the air on being heated, particularly when in the form of shavings or in the condition of vapour. At the ordinary temperature zinc does not decompose water—at any rate, if the metal is in a dense mass. But even at a temperature of 100° zinc begins little by little to decompose water; it easily displaces the hydrogen of acids at the ordinary temperature, and that of alkalies on being heated.

In this respect the action of zinc varies a great deal with the degree of its purity. Weak sulphuric acid (corresponding with the

---

it is necessary to prepare some salt of zinc in a pure state and transform it into carbonate, which latter is then distilled with charcoal; and, as thin sheets of zinc can only be obtained from very pure metal, they are frequently made use of in cases where pure zinc is required. In order to remove the arsenic from zinc, it was proposed to melt it and mix it with anhydrous magnesium chloride, by which means vapours of zinc chloride and arsenic chloride are formed. Perfectly pure zinc is made (V. Meyer and others) by decomposing, by means of the galvanic current, a solution of zinc sulphate to which an excess of ammonia has been added. The zinc used for Marsh's arsenic test (Chap. XIX.) is purified from As by fusing it with KNO_3 and then with $ZnCl_2$.

[9] Cornices and other architectural ornaments, remarkable for their lightness and beauty, are stamped out of sheet zinc. Zinc-roofing does not require painting, but it melts during a conflagration, and even burns at a strong heat. Many iron vessels, &c., are covered with zinc ('galvanised') in order to prevent them from rusting.

composition $H_2SO_4,8H_2O$) at the ordinary temperature does not act at all on chemically pure zinc, and even a stronger solution acts very slowly. If the temperature be raised, and particularly if the zinc be previously slightly heated, so as to cover the surface with a film of oxide, chemically pure zinc acts on sulphuric acid. Thus, for example, one cubic centimetre of zinc in sulphuric acid having a composition $H_2SO_4,6H_2O$ at the ordinary temperature in two hours only dissolves to the extent of 0·018 gram, and at a temperature of 100°, of about 3·5 grams. If we compare this slow action with that rapid evolution of hydrogen which occurs in the case of commercial zinc, we see that the influence of the impurities in the zinc is very great. Every particle of charcoal or iron introduced into the mass of the zinc, and likewise the connection of the zinc with a piece of another electro-negative metal, assist such a dissolution. The slowness of the action of sulphuric acid on pure zinc (and likewise on amalgamated zinc) may also be explained by the fact that a layer of hydrogen[10] collects on the surface of the metal, preventing contact between the acid and the metal.[10a]

---

[10] Veeren (1891) proved this by simple experiments, finding that *in vacuo* the solution proceeds far more rapidly for both pure and commercial zinc, and still more rapidly in the presence of oxidising agents (which absorb the hydrogen) like CrO_3 and H_2O_2.

[10a] The addition of cupric sulphate, or, better still, a few drops of platinic chloride (the metals become reduced), to the sulphuric acid greatly accelerates the evolution of the hydrogen, because in this case, as with commercial zinc, galvanic couples are formed locally by the copper or platinum and the zinc, under the influence of which the zinc rapidly dissolves. The action of acids on metallic zinc of various degrees of purity has been the subject of many investigations, particularly important with reference to the application of zinc in galvanic batteries, whilst some investigations have direct significance for chemical mechanics, although from many points of view the matter is not clear. I consider it useful to mention certain of these investigations.

Calvert and Johnson made the following series of observations on the action of sulphuric acid of various degrees of concentration on 2 grams of pure zinc during two hours. In the cold the concentrated acid, H_2SO_4, does not act, $H_2SO_4,2H_2O$ dissolves about 0·002 gram, but forms principally hydrogen sulphide, which is obtained also when the dilution reaches $H_2SO_4,7H_2O$, at which 0·035 gram of zinc is dissolved. When the acid is largely diluted with water, pure hydrogen begins to be disengaged. $H_2SO_4,2H_2O$ at 130° gives a mixture of hydrogen sulphide and sulphurous anhydride and dissolves 0·156 gram of zinc.

Bouchardat showed that if, in a vessel made of glass or sulphur, dilute sulphuric acid acting on a piece of zinc liberate one part of hydrogen, the same acid with the same piece of zinc in the same time will liberate 4 parts of hydrogen if the vessel be made of tin, with which the zinc forms a galvanic couple; in a leaden vessel 9 parts of hydrogen are set free, with one of antimony or bismuth 13 parts, with silver or platinum 33 parts, with copper 50 parts, and with iron 43 parts. Millon determined that if a salt of platinum is added to the dilute sulphuric acid (1 part of acid and 12 parts of water), the rapidity of the action on the zinc is increased 149 times, and by the addition of copper sulphate the action is rendered 45 times greater than that of pure sulphuric acid. The salts which are added are reduced to metals by the zinc, their contact serving to promote the reaction owing to the formation of local galvanic currents.

The action of zinc on acids, and the consequent formation of zinc salts, interfere with its application in many cases, particularly for the

According to the observations of Cailletet, if, at the ordinary pressure, sulphuric acid with zinc liberates 100 parts of hydrogen, then with a pressure of 60 atmospheres 47 parts will be liberated, and at a pressure of 120 atmospheres 1 part. With a reduced pressure under the receiver of an air-pump 168 parts are liberated. Helmholtz showed that a reduced pressure also exercises an influence on galvanic elements.

Debray, Löwel, and others showed that zinc liberates hydrogen and forms basic salts and zinc oxide with solutions of many salts; for instance, MCl_n, aluminium sulphate, and alum. Sodium and potassium carbonates scarcely act at all, because they form carbonates. The salts of ammonia act more strongly than those of potassium and sodium; the zinc remains bright. It is evident that this action is founded on the formation of double and basic salts.

The variation with concentration in the rate of the action of sulphuric acid on zinc (containing impurities) under otherwise uniform conditions is in evident connection with the electrical conductivity of the solution and its viscosity, although, when largely diluted, the action is almost proportional to the amount of acid in a known volume of the solution. Forging, casting the molten metal, and similar mechanical influences change the density and hardness of zinc, and also strongly influence its power of liberating hydrogen from acids. Kayander showed (1881) that when magnesium is submitted to the action of acids: (*a*) the action depends, not on the nature of the acid, but on its basicity; (*b*) the increase of the action is more rapid than the growth of the concentration; and (*c*) there is a decrease of action with an increase of the coefficient of internal friction and electrical conductivity.

Spring and Aubel (1887) measured the volume of hydrogen disengaged by an alloy of zinc and a small quantity of lead (0·6 per cent.), because the action of acids is then uniform. In order to deal with a known surface, spheres were taken (9·5 millimetres diameter) and cylinders (17 mm. diam.), the sides of which were covered with wax in order to limit the action to the end surfaces. During the commencement of the action of a definite quantity of acid the rapidity increases, attains a maximum, and then declines as the acid becomes exhausted. The results for 5, 10, and 15 per cent. of hydrochloric acid are given below. H denotes the number of cubic centimetres of hydrogen, D the time in seconds elapsing after the zinc spheres have been plunged into the acid.

At 15° were obtained:

	H = 50	100	200	400	600	800	1000
5 per cent.	D = 714	1152	1755	2731	3908	6234	15462
10 per cent.	D = 301	455	649	995	1573	2746	6748
15 per cent.	D = 106	151	233	440	826	1604	4289
At 35°:							
5 per cent.	D = 462	705	1058	1700	2525	4132	8499
10 per cent.	D = 96	148	239	460	835	1594	3735
15 per cent.	D = 44	64	112	255	505	1011	2457
At 55°:							
5 per cent.	D = 178	276	408	699	1164	2105	5093
10 per cent.	D = 34	60	113	258	491	970	2457
15 per cent.	D = 24	35	58	136	239	610	1593

In consequence of the complex character of the phenomenon, the authors themselves do not consider their determinations as being conclusive, and only give them a relative significance; and in this connection it is remarkable that hydrobromic acid under similar conditions (with an equivalent strength) gives a greater (from 2 to 5 times) rapidity of action than hydrochloric acid, but sulphuric acid a far smaller velocity (nearly 25 times smaller). It is also remarkable that during the reaction the metal becomes much more heated than the acid.

preservation of liquids either containing or capable of developing acid. For this reason zinc vessels ought not to be used for the preparation or preservation of food substances, as these often contain or yield acids which form poisonous salts with the zinc. Even ordinary water, containing carbonic acid, slowly attacks and corrodes zinc.

Finally divided zinc, or **zinc dust**, obtained in the distillation of the metal when the receiver is not heated up to the melting-point, on account of its presenting a large surface of contact and containing foreign matter (particularly zinc oxide), has in the highest degree the property of acting on acids, and even water, which it easily decomposes, particularly if slightly heated. On this account zinc dust is often used in laboratories and factories as a reducing agent. A similar influence of the finely divided state is also noticed in other metals—for instance, copper and silver—which again shows the close connection between chemical and physico-mechanical phenomena. We must first of all turn to this close connection for an explanation of the widespread application of zinc in galvanic batteries, where the chemical (latent, potential) energy of the acting substances is transformed into (evident, kinetic) galvanic energy, and through this latter into heat, light, or mechanical work.

Hermann and Stromeyer, in 1819, showed that **cadmium** is almost always found with zinc, and in many respects resembles it. When distilled the cadmium volatilises sooner, because it has a lower boiling-point. Sometimes the zinc dust obtained by the first distillation of zinc contains as much as 5 per cent. of cadmium. When zinc blende, containing cadmium, is roasted, the zinc passes into the state of oxide, and the cadmium sulphide in the ore oxidises to cadmium sulphate, $CdSO_4$, which resists tolerably well the action of heat; therefore if roasted zinc blende be washed with water, a solution of cadmium sulphate will be obtained, from which it is very easy to prepare metallic cadmium. Hydrogen sulphide may be used for separating cadmium from its solutions; it gives a **yellow precipitate of cadmium sulphide**, CdS (according to the equation $CdSO_4+H_2S=H_2SO_4+CdS$),[11] which, on account of its characteristic colour, is used as a pigment.[11a]

It may be mentioned that zinc dust or zinc itself, when heated with hydrated lime and similar hydrates, disengages hydrogen: this method has even been proposed for obtaining hydrogen for filling war balloons.

[11] It may be here remarked that sulphate of zinc (especially in the presence of mineral acids, which decompose ZnS) does not give a precipitate of sulphide of zinc, or is only slightly precipitated by sulphuretted hydrogen.

[11a] Sulphide of cadmium appears in two varieties of a similar chemical but different physical character: one is of a lemon colour, and the other red. Kloboukoff (1890) studied the physical properties of these varieties more closely. The sp. gr. of the former

Cadmium sulphide, when strongly heated in air, leaves cadmium oxide, from which the metal may be obtained in precisely the same way as in the case of zinc.

Cadmium is a white metal, and when freshly cut is almost as white and lustrous as tin. It is so soft that it may be easily cut with a knife, and so malleable that it can be easily drawn into wire, rolled into sheets, &c. Its specific gravity is 8·67, melting-point 320°, boiling point 770°; its vapours burn, forming a brown powder of the oxide.[12] Next to mercury it is the most volatile metal; hence Deville determined the density of its vapours compared with hydrogen, and found it to be equal to 57·1; therefore the molecule contains **one atom** whose weight is 112. V. Meyer found the like for zinc; the molecule of mercury also contains one atom.

Mercury resembles zinc and cadmium in many respects, but presents that distinction from them which is always noticed in all the heaviest metals (with regard to atomic weight and density) compared with the lighter ones—namely, that it oxidises with more difficulty, and its compounds are more easily decomposed.[12a] Besides compounds of the

---

is 3·906, and that of the latter 4·513. They belong to different crystallographic systems. The first variety may be converted into the second by friction or pressure, but the second cannot be converted into the first variety by these means.

[12] Of the compounds of cadmium very closely allied to the compounds of zinc, we must mention **cadmium iodide**, CdI_2, which is used in medicine and photography. This salt crystallises very well; it is prepared by the direct action of iodine, mixed with water, on metallic cadmium. One part of cadmium iodide at 20° requires for its solution 1·08 part of water. Cadmium chloride at the same temperature requires 0·71 part of water to dissolve it, so that the iodine compound of this metal is less soluble than the chloride, whilst the reverse relation holds in the case of the corresponding compounds of the alkali or alkaline earth metals. *Cadmium sulphate* crystallises well, and has the composition $3CdSO_4,8H_2O$, thus differing from zinc sulphate.

Cadmium oxide is soluble, although sparingly, in alkalies, but in the presence of tartaric and certain other acids the alkaline solution of cadmium oxide does not change when boiled, whilst a *diluted* solution in that case deposits cadmium oxide: this may also serve for separating zinc from cadmium. The latter is precipitated from its salts by zinc, so that from an alloy of zinc and cadmium, acids first of all extract the zinc. Cadmium is in all respects less energetic than zinc. Thus, for instance, it decomposes water with difficulty, and only when strongly heated. It even acts but slowly on acids, but then displaces hydrogen from them. It is necessary here to call attention to the fact that for alkali and alkaline earth metals (of the even series) the highest atomic weight determines the greatest energy; but cadmium (of the uneven series), whilst having a larger atomic weight than zinc, is less energetic. The salts of cadmium are colourless, like those of zinc. De Schulten obtained a crystalline oxychloride, Cd(OH)Cl, by heating marble with a solution of cadmium chloride in a sealed tube at 200°. It is notable that even very dilute solutions (0·2 per cent.) of $CdCl_2$ (and also of $CdBr_2$, $CuCl_2$, $HgCl_2$, &c.), are precipitated by an excess of strong sulphuric acid, so that a reagent for detecting traces of any chloride may be prepared by mixing 1 vol. of a 10 per cent. solution of $CdSO_4$ with 10 vols. of H_2SO_4.

[12a] According to its atomic weight, mercury follows gold in the periodic system, just as cadmium follows silver and zinc follows copper:—

usual type RX_2, it also gives those of the lower type, RX, which are unknown for zinc.[13] Mercury therefore gives salts of the composition HgX (mercurous salts) and HgX_2 (mercurous salts), the oxides having the formulæ Hg_2O and HgO respectively.

Mercury is found **in nature** almost exclusively in combination with sulphur (like zinc and cadmium, but is still rarer than them) in the form known as cinnabar, HgS (Chap. XX., note 29). It is far more rarely met with in the native or metallic condition, and this in all probability has been derived from cinnabar. Mercury ore is found only in a few places—namely, in Spain (in Almaden), in Illyria, Japan, Peru, and California. About the year 1880 Minenkoff discovered a rich bed of cinnabar in the Bahmout district (near the station of Nikitovka), in the government of Ekaterinoslav, so that now Russia even exports mercury to other countries. Cinnabar is now also being worked in Daghestan in the Caucasus. Mercury ores are easily reduced to metallic mercury, because the combination between the metal and the sulphur is one of but little stability. Oxygen, iron, lime, and many other substances, when heated, easily destroy the combination. If iron is heated with cinnabar, iron sulphide is formed; if cinnabar is heated with lime, mercury and calcium sulphide and sulphate are formed, $4HgS + 4CaO = 4Hg + 3CaS + CaSO_4$. On being heated in the air, or roasted, the sulphur burns, oxidises, forming sulphurous anhydride, and vapours of metallic mercury are formed. Mercury is more easily distilled than all other metals, its boiling-point being about 351°, and its separation from natural admixtures after decomposition by one of the above-mentioned methods is therefore effected at the expense of a comparatively small amount of heat. The mixture of mercury vapour,

Ni = 59	Cu = 63	Zn = 65
Pd = 106	Ag = 108	Cd = 112
Pt = 195	Au = 197	Hg = 200

Eventually we shall see the near relation of platinum, palladium, and nickel, and also of gold, silver, and copper, but we shall now point out the parallelism between these three groups. The relations between the physical and also the chemical properties are here strikingly similar. Nickel, palladium, and platinum are very difficult to fuse (far more so than iron, ruthenium, and osmium, which stand before them). Copper, silver, and gold melt far more easily in a strong heat than the three preceding metals, and zinc, cadmium, and mercury melt still more easily. Nickel, palladium, and platinum are very slightly volatile; copper, silver, and gold are more volatile; and zinc, cadmium, and mercury are among the most volatile metals. Zinc oxidises more easily than copper, and is reduced with more difficulty, and the same is true for mercury as compared with gold. These properties for cadmium and silver are intermediate in the respective groups. Relations of this kind clearly show the reality of the periodic law.

[13] Thus thallium, lead, and bismuth, following mercury according to their atomic weights, form, besides compounds of the highest types, TlX_3, PbX_4, and BiX_5, also the lower ones TlX, PbX_2, and BiX_3. Cadmium, as the nearest analogue of Hg, also gives a lower oxide, formed by calcining the oxalate.

air, and products of combustion obtained is cooled in tubes (by water or air), in which the mercury condenses as liquid metal.[14] About 4,000 tons of mercury are produced yearly by the mines of the world.

Mercury, as everybody knows, is a liquid metal at the ordinary temperature. In its lustre and whiteness it resembles silver.[15] It boils at +357°. At −39° mercury is transformed into a malleable crystalline metal; at 0° its specific gravity is 13·596, and in the solid state at −40° it is 14·39.[16] Mercury does not change in the air—that is to say, it does not oxidise at the ordinary temperature—but at a temperature approaching the boiling-point, as was stated in the Introduction, it oxidises, forming mercuric oxide. Both metallic mercury and its compounds in general produce salivation, trembling of the hands, and other unhealthy symptoms which are found in the workmen exposed to the influence of mercurial vapours[17] or the dust of its compounds.

As many of the compounds of mercury decompose on being heated

---

[14] During the condensation of the vapours of mercury in works, a part forms a black mass of finely divided particles, which gives metallic mercury when worked up in centrifugal machines, or when compressed or re-distilled. In mercury we observe a tendency to split up easily into the finest drops, which are difficult to unite into a dense mass. It is sufficient to shake up mercury with nitric and sulphuric acids in order to produce such a mercury *powder*. The mercury separated (for instance, reduced by substances like sulphurous anhydride) from solutions forms such a powder. According to the experiments of Nernst, this disintegrated mercury when entering into reactions develops more heat than the dense liquid metal; that is say, the work of disintegration reappears in the form of heat. This example is instructive in considering thermo-chemical deductions.

[15] Mercury may sometimes be obtained in a perfectly pure state from works (in iron bottles holding about 35 kilos), but after being used in laboratories (for baths, calibration, &c.) it contains impurities. It may be purified mechanically in the following way: a paper filter with a fine hole (pricked with a needle) is placed in a glass funnel and into it is poured mercury, which slowly trickles through the hole, leaving the impurities upon the filter. Sometimes it is squeezed through chamois leather or through a block of wood (as in the well-known experiment with the air-pump). It may be purified from many metals by contact with dilute nitric acid, if small drops of mercury are allowed to pass through a long column of it (from the fine end of a funnel); or by shaking it up with sulphuric acid in air. Mercury may be purified by the action of an electric current, if it be covered with a solution of $HgNO_3$. But the complete purification of mercury for barometers and thermometers can only be attained by distillation, best in a vacuum (the vapour pressure of mercury is given in Chap. II., note 27). For this purpose Weinhold's apparatus is most often used. The principle of this apparatus is very ingenious, the distillation being effected in a Torricellian vacuum continuously supplied with fresh mercury, while the condensed mercury is continuously removed. This process of distillation requires very little attention, and gives about one kilo of pure mercury per hour.

[16] If the volume of *liquid* mercury at 0° be taken as 1000000, then, according to the determinations of Regnault (re-calculated by me in 1875), at $t°$ it will be $1000000 + 180{\cdot}1t + 0{\cdot}02t^2$, or $1000000 + 181{\cdot}6t + 0{\cdot}08t^2$ according to Tuson.

[17] The alchemists called mercury 'mercurii,' and this name has been adopted in science instead of the popular term 'quicksilver.'

—for instance, the oxide or carbonate[18]—and as zinc, cadmium, copper, iron, and other metals separate mercury from its salts,[19] it is evident that mercury has less chemical energy than the metals already described, even than zinc and cadmium. Nitric acid, when acting on *an excess* of mercury at the ordinary temperature, gives mercurous nitrate, $HgNO_3$.[20] The same acid, under the influence of heat and when in excess (nitric oxide being liberated), forms mercuric nitrate, $Hg(NO_3)_2$. This,[21] both in its composition and properties, resembles the salts of zinc and cadmium. Dilute sulphuric acid does not act on mercury, but strong sulphuric acid dissolves it, with *evolution of sulphurous anhydride* (not hydrogen), and on being slightly heated with an excess of mercury it forms the sparingly soluble mercurous sulphate, Hg_2SO_4; but if mercury is strongly heated with an excess of the acid, the mercuric salt, $HgSO_4$,[22] is formed. Alkalies do not act on mercury, but the non-metals chlorine, bromine, sulphur, and phosphorus easily combine with it. They yield, like the acids, two series of compounds, HgX and HgX_2. The oxygen compound of the first series is the suboxide of mercury, or mercurous oxide, Hg_2O, and

---

[18] All salts of mercury, when mixed with sodium carbonate and heated, decompose, forming carbonic anhydride, oxygen, and vapours of mercury.

[19] Spring (1888) showed that solid dry HgCl is gradually decomposed in contact with metallic copper. According to the determinations of Thomsen, the formation of a gram of mercurial compounds from their elements develops the following amounts of heat (in thousands of units): Hg_2+O, 42; Hg + O, 31; Hg + S, 17; Hg + Cl, 41; Hg + Br, 34; Hg + I, 24; $Hg+Cl_2$, 63; $Hg+Br_2$, 51; $Hg+I_2$, 34; $Hg+C_2N_2$, 19. These numbers are less than the corresponding ones for potassium, sodium, calcium, barium, and for zinc and cadmium—for instance, Zn + O, 85; $Zn+Cl_2$, 97; $Zn+Br_2$, 76; $Zn+I_2$, 49; $Cd+Cl_2$, 93; $Cd+Br_2$, 75; $Cd+I_2$, 49.

[20] This salt easily forms the crystallo-hydrate $HgNO_3,H_2O$, corresponding with ortho-nitric acid, H_3NO_4 (the terms ortho-, pyro-, and meta-acids are explained in the chapter on Phosphorus), with the substitution of Hg for H. In an aqueous solution this salt can only be preserved in the presence of free mercury, otherwise it forms basic salts of the oxide, which will be mentioned hereafter.

[21] Mercuric nitrate, $Hg(NO_3)_2,8H_2O$, crystallises from a concentrated solution of mercury in an excess of boiling nitric acid. Water decomposes this salt; at the ordinary temperature crystals of a basic salt of the composition $Hg(NO_3)_2,HgO,2H_2O$ are formed, and with an excess of water the insoluble yellow basic salt $Hg(NO_2)_2,H_2O,2HgO$. These three salts correspond with the type of ortho-nitric acid, $(H_3NO_4)_2$, in which mercury is substituted for 1, 2, and 3 times H_2.

[22] To obtain the mercuric salt a large excess of strong sulphuric acid must be taken and strongly heated. With a small quantity of water colourless crystals of $HgSO_4,H_2O$ may be obtained. An excess of water, especially when heated, forms the basic salt (as in note 21), $HgSO_4,2HgO$, which corresponds with trihydrated sulphuric acid, $SO_3+3H_2O=S(OH)_6$, with the substitution of H_6 by 3Hg, which in mercuric salts are equivalents. Le Chatelier (1888) gives the following ratios between the amounts of equivalents per litre:

$HgSO_4$	0·318	0·890	1·80	2·02
SO_3	0·752	1·42	2·10	2·40

—that is, the relative amount of free acid decreases as the strength of the solution increases.

that of the second order the oxide HgO, mercuric oxide. The chlorine compound corresponding with the suboxide is HgCl (calomel), and with the oxide $HgCl_2$ (corrosive sublimate or mercuric chloride). In the compounds HgX, mercury is univalent and resembles the metals of the first group, and more especially silver. In the mercuric compounds there is an evident resemblance to those of magnesium, cadmium, &c. Here the atom of mercury is bivalent, as in the type RX_2.[23] Every

---

[23] The molecular weight of calomel was a contested point of great interest in chemistry during the eighties and the beginning of the nineties of the last century, because in those days there were many chemists who argued from the fact of C being generally quadrivalent in the carbon compounds (forgetting CO), that the atomicity of the elements (Chap. X., note 1) must be a constant, fundamental, and unchangeable property of the elementary atoms, and that therefore Hg must be exclusively divalent, because it gives mercury ethyl, $Hg(C_2H_5)_2$, and corrosive sublimate, $HgCl_2$, about the molecular weight of which there could be no doubt (judging by the reactions and the vapour densities). But as calomel, HgCl, is volatile, and its vapour density (about 118 if $H = 1$) indicates its molecular composition to be HgCl, it is necessary to regard the mercury in it as univalent. Endeavours were made to explain this by saying that the molecule of calomel contains Hg_2Cl_2, and that its vapour does not contain true calomel, Hg_2Cl_2, but only the products of its decomposition, corrosive sublimate and mercury, $Hg_2Cl_2 = HgCl_2 + Hg$. This would render it possible to consider mercury as divalent in all its compounds, because calomel would then be regarded as a compound of two residues (radicles), HgCl, of corrosive sublimate in which mercury is diatomic (like two residues of CH_4 in C_2H_6, Chap. VIII.). Moreover, the vapour density of calomel (under its assumed decomposition) should, indeed, be about 118, for that of corrosive sublimate is about 136, and that of mercury 100, so that the value for calomel would be half their sum. Efforts were made, and with some success, to confirm this hypothesis (and similar ones were often adopted for other elements in those days) by experiment in order to corroborate a false theory, namely, the constancy of the atomicity of the elements. The researches of V. Meyer and Harris (1894) were particularly convincing in this respect. They showed (1) that more mercury vapour than chlorine is diffused through the pores of an earthenware vessel in which calomel is volatilised at 465°, so that some corrosive sublimate must have remained in the vessel; and (2) that a hot piece of KHO introduced into the vapour of calomel gives yellow oxide of mercury, and not the black suboxide, whence they concluded that the vapour contains no calomel, but only a mixture of the vapours of corrosive sublimate and mercury. The evidence given by these experiments is doubtful, first, because the difference between the rates of diffusion of the vapours of Hg and HgCl is infinitesmal (for the vapour densities are very much alike, and their square roots still more so); and, secondly, the suboxide of mercury (see text) and the compounds corresponding to it are unstable and easily pass into (even under the action of light) the oxide and metallic mercury. So that there is every reason for supposing that a portion of the calomel HgCl exists in the vapour and a portion decomposes (a state of equilibrium sets in); but there is no cause for assuming entire decomposition, for there can be no doubt that there are vapours and gases whose molecules prove the possibility of elements having more than one form of atomicity, for instance, CO and CO_2; N_2O, NO, and NH_3; PCl_3 and PCl_5 or PF_5, &c. So that, speaking in general terms, a constant atomicity in the elements is not in the nature of things, and this apparent constancy can only be looked upon as a method of former days, having its historical interest as a means of incentive to research. Concerning the molecular weight of calomel in particular, there is no foundation for assuming this to be other than HgCl, according to the results of direct experiment; and if it is found that its vapour contains Hg and $HgCl_2$ (*in toto* or in part), this does not interfere with the modern chemical notions of the variability of atomicity.

soluble mercurous compound (corresponding with the type of the suboxide of mercury), HgX, forms a white precipitate of calomel, HgCl, with hydrochloric acid or a metallic chloride, because HgCl is very slightly soluble in water, $HgX + MCl = HgCl + MX$. With soluble mercuric compounds, HgX_2, hydrochloric acid and metallic chlorides do not form a precipitate, because corrosive sublimate, $HgCl_2$, is soluble in water. Alkali hydroxides precipitate the yellow mercuric oxide from a solution of HgX_2, and the black mercurous oxide from one of HgX. Potassium iodide forms a dirty greenish precipitate, HgI, with mercurous salts, HgX, and a red precipitate, HgI_2, with the mercuric salts, HgX_2. These reactions distinguish the mercuric from the mercurous salts, which latter represent the transition from the mercuric salts to mercury itself, $2HgX = Hg + HgX_2$. The salts, HgX, as well as HgX_2, are reduced by nascent hydrogen (e.g., from $Zn + H_2SO_4$), by such metals as zinc and copper, and also by many other reducing agents—for example, hypophosphorous acid, the lowest grade of oxidation of phosphorus, by sulphurous anhydride, stannous chloride, &c. Under the action of these reagents the mercuric salts are generally first transformed into the mercurous salts, and the latter then reduced to metallic mercury. This reaction is so delicate that it serves to detect the smallest quantity of mercury; for instance, in cases of poisoning, the mercury is detected by immersing a copper plate in the solution to be tested, the mercury being then deposited upon it (more readily on passing a galvanic current). The copper plate, on being rubbed, shows a silvery white colour; on being heated, it yields vapours of mercury, and then again assumes its original red colour (if it does not oxidise). The mercurous compounds, HgX, under the action of oxidising agents, even air, pass into mercuric compounds, especially in the presence of acids (otherwise a basic salt is produced), $2HgX + 2HX + O = 2HgX_2 + H_2O$; but the mercuric compounds, when in contact with mercury, undergo change more or less readily, and turn into mercurous compounds, $HgX_2 + Hg = 2HgX$. For this reason, in order to preserve solutions of mercurous salts, a little mercury is generally added to them.

The lowest oxygen compound of mercury—that is, **mercurous oxide**, Hg_2O—apparently only exists in a transient form, for the substance precipitated in the form of a black mass by the action of alkalies on a solution of mercurous salts decomposes on keeping (especially in sunlight) into the yellow mercuric oxide and metallic mercury, and then acts as a simple mechanical mixture of oxide, HgO, with mercury (Guibourt, and others). The other compound of mercury with oxygen is already known to us as **mercuric oxide**, HgO, obtained in the form of a red crystalline substance by the oxidation of mercury in the air, and precipitated as a yellow powder by the action of sodium hydroxide on solutions of salts of the type HgX_2. In this case it is amorphous and more amenable to the action of various reagents (Chap. XI., note 32) than when it is in the crystalline state. Indeed, on trituration, the red oxide is changed into a powder of a yellow colour. It is very sparingly soluble in water, and forms an alkaline solution which precipitates magnesia from the solution of its salts.

Mercury combines directly with chlorine, and the first product of combination is **calomel** or mercurous chloride, $HgCl$. This is obtained, as above stated, in the form of a white precipitate by mixing solutions of mercurous salts with hydrochloric acid or with metallic chlorides. A precipitate of calomel is also obtained by reducing a boiling aqueous solution of corrosive sublimate, $HgCl_2$, with sulphurous anhydride. It is likewise produced by heating corrosive sublimate with mercury.[23a] Calomel may be distilled. In the solid state its specific gravity is 7·0; it crystallises in rhombic prisms, is colourless, but has a yellowish reflection, turns brown from the action of light, and when boiled with hydrochloric acid decomposes into mercury and corrosive sublimate. It is used as a strong purgative. **Corrosive sublimate** or mercuric chloride, $HgCl_2$, can be obtained from or converted into calomel by many methods.[24] An excess of chlorine (for instance, *aqua regia*) converts calomel and also mercury into corrosive sublimate. It owes its name corrosive sublimate to its volatility, and, in medicine up to the present day, it is termed *Mercurius sublimatus seu corrosivus*. The vapour density, compared with that of hydrogen, is 135, so that its molecule is $HgCl_2$. It forms colourless prismatic crystals of the rhombic system, boils at 307°, and is soluble in alcohol. It is usually prepared by subliming a mixture of mercuric sulphate with common salt, $HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2$. Owing to its being soluble in water, and reacting on albuminous substances, corrosive sublimate is a strong poison. It

---

[23a] Calomel (in Japanese, *keyfun*) has been prepared in Japan (and China) for many centuries, by heating mercury in clay crucibles with sea salt, which contains $MgCl_2$ and gives HCl. The vapour of the mercury reacts with this HCl and the oxygen of the air and forms calomel: $2Hg + 2HCl + O = 2HgCl + H_2O$. The calomel collects on the lid of the crucible in the form of a sublimate (Divers, 1894).

[24] $HgCl_2$ is partially converted into calomel even in the act of dissolving in ordinary water, especially under the action of light. The reduction of $HgCl_2$ into $HgCl$ proceeds with still greater facility under the action of light in the presence of salts of oxalic acid (Shoras, 1870). According to Kistiakoffsky (1902) a double salt acts here which may be obtained by dissolving mercuric oxalate, HgC_2O_4, in a solution of KCl, and has the composition of a double salt of HCl and $C_2H_2O_4$ with the metals K and Hg.

is used as a disinfectant, especially in surgical operations, and for preserving natural history specimens and for embalming. Corrosive sublimate combines with mercuric oxide, forming an oxychloride or basic salt,[24a] of the composition $HgCl_2,2HgO$ (magnesium and zinc form similar compounds). This compound is obtained by mixing a solution of corrosive sublimate with either mercuric oxide or a solution of sodium bicarbonate. In general, with both mercurous and mercuric salts, there is a marked tendency to form basic salts.[25]

[24a] As feebly energetic bases (like, for instance, the oxides MgO, ZnO, PbO, CuO, Al_2O_3, Bi_2O_3, &c.), mercuric oxide and mercurous oxide easily give basic salts, which are usually directly formed by the action of water on the normal salt, according to the general equation (for mercuric compounds, RX_2):

$$\underset{\text{neutral salt}}{nRX_2} + \underset{\text{water}}{mH_2O} = \underset{\text{acid}}{2mHX} + \underset{\text{basic salt}}{(n-m)RX_2mRO}$$

or else are produced directly from the normal salt and the oxide or its hydroxide. Thus mercurous nitrate, when treated with water, forms basic salts of the composition $6(HgNO_3),Hg_2O,H_2O$; $2(HgNO_3),Hg_2O,H_2O$, and $3(HgNO_3),Hg_2O,H_2O$, the first two of which crystallise well. Our present knowledge of basic salts is not sufficiently complete to admit of generalisations. However, it is already possible to view the subject in the following aspects: (1) basic salts are principally formed from feeble bases: (2) certain metals (mentioned above) form them with particular ease, so that one of the causes of the formation of many basic salts must depend on the property of the metal itself; (3) those bases which readily form basic salts as a rule also readily form double salts; (4) in the formation of basic salts, as also everywhere in chemistry, where sufficient facts have accumulated, we clearly see the conditions of equally balanced heterogeneous systems, such as we saw, for instance, in the formation of double salts, crystallo-hydrates, &c.

The mercuric salts often form double salts, and mercuric chloride easily combines with ammonia, forming $Hg(NH_4)_2Cl_4$, or in general $HgCl_2,nMCl$. If a mixture of mercurous and potassium sulphates is dissolved in dilute sulphuric acid, the solution readily yields large colourless crystals of a double salt of the composition $K_2SO_4,3HgSO_4,2H_2O$. Boullay obtained crystalline compounds of mercuric chloride with hydrochloric acid, and of mercuric iodide with hydriodic acid; and Thomsen describes the compound $HgBr_2,HBr,4H_2O$ as a well-crystallised salt, melting at 13°, and having, in a molten state, a specific gravity 3·17 and a high index of refraction. Moreover, the capacity of salts for forming basic compounds has been considerably cleared up since the investigations (by Würtz, Lorenz, and others) of glycol, $C_2H_4(OH)_2$ (and of polyatomic alcohols resembling it), because the ethers $C_2H_4X_2$, corresponding with it, are capable of forming compounds of the composition $C_2H_4X_2,nC_2H_4O$.

On the other hand, there is reason to think that the property of forming basic salts is connected with the polymerisation of bases, especially colloidal ones (see the chapters on Silica, Lead Salts, and Tungstic Acid). This still offers a vast and fruitful field for theoretical and experimental research, to which the beginner's attention ought certainly to be drawn.

[25] **Mercuric iodide**, HgI_2, is obtained first as a yellow, and then as a red, precipitate on mixing solutions of mercuric salts and potassium iodide, and is soluble in an excess of the latter (in consequence of the formation of the double salt, $HgKI_3$) or of ammonium chloride (for a similar reason), &c. It crystallises at the ordinary temperature in square prisms of a red colour. On being heated to 126°, these change into yellow rhombic crystals, isomorphous with mercuric chloride. This yellow form of mercuric iodide is very unstable, and when cooled and triturated easily assumes the more stable red form again When fused, a yellow liquid is obtained. This is an instance of dimorphism. After the

Mercury has a remarkable power of forming very unstable compounds with ammonia, in which the mercury replaces the hydrogen, and, if a mercuric compound be taken, its atom occupies the place of two atoms of the hydrogen in the ammonia. Thus Plantamour and Hirtzel showed that when precipitated mercuric oxide, dried at a gentle heat, is continuously heated (up to 100°–150°) in a stream of dry ammonia, it leaves a brown powder of **mercuric nitride**, N_2Hg_3, according to the equation: $3HgO + 2NH_3 = N_2Hg_3 + 3H_2O$.[25a] This substance, which is attacked by water, acid, and alkalies (giving a white powder), is very explosive when struck or rubbed, and evolves nitrogen, proving that the bond between the mercury and the nitrogen is very feeble.[26] By the action of liquefied ammonia on yellow mercuric

addition of caustic potash, a solution of HgI_2 in KI (there is no precipitate) gives NHg_2I with even traces of ammonia. This is NH_4Cl with the substitution of H_4 by Hg_2 and Cl by I, according to the equation: $2HgI + NH_3 + KHO = NHg_2I + 3KI + 3H_2O$, and this reaction is employed for detecting the presence of ammonia (Nessler's test).

Mercuric cyanide, $Hg(CN)_2$, forms one of the most stable metallic cyanides. It is obtained by dissolving mercuric oxide in prussic acid, and by boiling Prussian blue with water and mercuric oxide, ferric oxide being then obtained in the precipitate. Mercuric cyanide is a colourless crystalline substance, soluble in water, and distinguished by its great stability; sulphuric acid does not liberate prussic acid from it, and even caustic potash does not remove the cyanogen (a complex salt is probably produced), but the halogen acids disengage HCN. Like the chloride, it combines with mercuric oxide, forming the oxycyanide, $Hg_2O(CN)_2$, and it shows a very marked tendency to form double compounds—for example, $K_2Hg(CN)_4$. The alkali chlorides and iodides form similar compounds—for instance, the salt $HgKI(CN)_2$ crystallises very well, and is produced by directly mixing solutions of potassium iodide and mercuric cyanide.

Wells (1889) and Vare obtained and investigated many such double salts, and showed the possibility of the formation, not only of $HgCl_2,MCl$ and $HgCl_2,2MCl$, where M is a metal of the alkalies—for example, Cs—but also of $HgCl_2,3MCl$, $2(HgCl_2),MCl$, and in general $nHgX_2,mMX$, where X stands for various haloids.

[25a] See Chap. XIX., note 6a: Hg_3P_2. In studying the metallic nitrides it is necessary to keep the corresponding phosphides in mind.

[26] Hg_3N_2 is similar in composition to Mg_3N_2, &c. (Chap. XIV.). The readiness with which mercuric nitride explodes shows that the connection between the nitrogen and the mercury is very unstable, and explains the circumstance that the so-called **mercury fulminate**, or **fulminating mercury**, is an example of explosives in general. This substance is prepared in large quantities for explosive mixtures; it enters into the composition of percussion caps, which explode when struck, and ignite gunpowder. Mercury fulminate was discovered by Howard, and from that time has been prepared in the following way: one part of mercury is dissolved in twelve parts of nitric acid of sp. gr. 1·36, and when the whole of the mercury is dissolved, 5·5 parts of 90 per cent. alcohol are added, and the mass is shaken. A reaction then commences, accompanied by a rise in temperature due to the oxidation of the alcohol. As a matter of fact, many oxidation products are produced during the action of the nitric acid on the alcohol (glycollic acid, ethers, &c.). When the reaction becomes tolerably vigorous, the same quantity of alcohol is added as at the commencement, when a grey precipitate of the fulminate separates. This salt has the composition $C_2Hg(NO_2)N$. It explodes when struck or heated. The mercury in it may be replaced by other metals—for instance, copper or zinc, and also silver. The silver salt, $C_2Ag_2(NO_2)N$, is obtained in a precisely analogous manner, and is even more explosive. Under the action of alkali chlorides, only half the silver is

oxide, Weitz also obtained an explosive compound, dimercurammonium hydroxide, N_2Hg_4O, which corresponds with an ammonium oxide, $(NH_4)_2O$, in which the whole of the hydrogen is replaced by mercury. A solution of ammonia reacts with mercuric oxide, forming the hydroxide, $NHg_2{\cdot}OH$, to which a whole series of salts, NHg_2X (see note 25), correspond; these are generally insoluble in water and capable of decomposing with an explosion. But salts of the same type, but with one atom of mercury, NH_2HgX, are more frequently and more easily formed; they were principally studied by Kane, although known much earlier. Thus, if ammonia is added to a solution of corrosive sublimate (or, still better, in reverse order), a precipitate is obtained

replaced by the alkali metal, but if the whole of the silver is replaced by an alkali metal, the salt decomposes. This is evidently because combinations of this kind proceed in virtue of the formation of substances in which mercury, and metals akin to it, are connected in an unstable way with nitrogen. Potassium and other light metals are incapable of entering into such connection, so that the substitution of potassium for mercury entails the splitting-up of the combination. Investigations of the fulminates were carried out by Gay-Lussac and Liebig, but only the investigations of L. N. Shishkoff fully cleared up the composition of these substances and their relation to the other carbon compounds. Shishkoff showed that fulminates correspond with the nitro-acid, $C_2H_2(NO_2)N$. The explosiveness of the group depends partly on its containing at the same time NO_2 and carbon; we already know that all such nitrogen compounds are explosive. If we imagine that the NO_2 is replaced by hydrogen, we shall have a substance of the composition C_2H_3N. This is acetonitrile—that is, acetic acid + $NH_3 - 2H_2O$, or ethenyl nitrile, as shown in Chap. VI. The formation of an acetic compound by the action of nitric acid on alcohol is easily understood, because acetic acid is produced by the oxidation of alcohol, and the production of the elements of ammonia, indispensable for the formation of a nitrile, is accounted for by the fact that nitric acid, under the action of reducing substances, in many cases forms ammonia (Chap. VI., note 27). Moreover, a certain analogy has been found between fulminating acid and hydroxylamine, but details upon this subject must be looked for in works on organic chemistry. The explosiveness of fulminating mercury, the rapidity of its decomposition (gunpowder, and even guncotton, burn more slowly and explode less violently), and the force of its explosion are such that a small quantity (loosely covered) will shatter massive objects.

The investigations of Abel on the communication of explosion from one substance to another are remarkable. If guncotton is ignited in an open space, it burns quietly; but if fulminating mercury be exploded by the side of it, the decomposition of the guncotton will be effected instantaneously, and it then shatters the objects upon which it lies, so rapid is the decomposition. Abel explains this by supposing that the explosion of the fulminating salt brings the molecules of guncotton into a uniform or as it were harmonious state of vibration, which causes the rapid decomposition of the whole mass. This rapid decomposition of explosive substances defines the distinction between explosion and combustion. Besides this, Berthelot showed that from that form of powerful molecular concussion which takes place during the explosion of fulminating mercury, the state of strain and stability of equilibrium of substances which are endothermal, or capable of decomposing with the disengagement of heat—for instance, cyanogen, nitro- compounds, nitrous oxide, &c.—is generally destroyed. Thorpe showed that carbon bisulphide, CS_2, also an endothermal substance, decomposes into sulphur and charcoal, when fulminating mercury is exploded in contact with it. Such experiments with explosives thus offer a subject of inexhaustible interest, and, notwithstanding their danger, are eagerly prosecuted by men of science.

known as white precipitate (*Mercurius præcipitatus albus*) or **mercurammonium chloride**, NH_2HgCl, which may also be regarded not only as sal-ammoniac with the substitution of H_2 by mercury, but also as HgX_2, where one X represents Cl and the other X represents the ammonia radicle, $HgCl_2 + 2NH_3 = NH_2{\cdot}HgCl + NH_4Cl$. When heated, mercurammonium chloride decomposes, yielding mercurous chloride; when heated with dry hydrochloric acid it forms ammonium chloride and mercuric chloride. Other simple and double salts of mercurammonium, NH_2HgX, are also known. Pesci (1890) showed that all the compounds HgH_2NX may be regarded as compounds of the above-named Hg_2NX with NH_4X because their sum equals $2HgH_2X$.[26a]

Mercury as a liquid metal is capable of dissolving other metals and forming solid and liquid metallic solutions or alloys. These are generally called **amalgams**. The formation of these solutions is often accompanied by the development of a large amount of heat, for instance, when potassium and sodium are dissolved (Chap. XII., note 39); but sometimes heat is absorbed, as, for instance, when lead is dissolved. It is evident that phenomena of this kind are very similar to the phenomena accompanying the dissolution of salts and other substances in water, but here it is easy to demonstrate what is far more difficult to observe in the case of salts: the solution of metals in mercury is accompanied by the formation of definite chemical compounds of the mercury with the metals dissolved. This is shown by the fact that when pressed (best of all in chamois leather) such solutions leave solid, definite compounds of mercury with metals. It is, however, very difficult to obtain them in a pure state, on account of the difficulty of separating the last traces of mercury, which is mechanically distributed between the crystals of the compounds. Nevertheless, in many cases such compounds have undoubtedly been obtained, and their existence is clearly shown by the evident crystalline structure and characteristic appearance and fixed melting-point, which

---

[26a] The capacity for replacing hydrogen in chloride of ammonium by metals also belongs to Zn and Cd. Kvasnik (1892), by the action of ammonia upon alcoholic solutions of $CdCl_2$ and $ZnCl_2$, obtained substances of the general formula $M(NH_3Cl)_2$, formed as it were from two molecules of sal-ammoniac by the substitution of two atoms of hydrogen by a diatomic metal. These substances appear as white finely crystalline powders. Under the action of heat half the ammonia passes off, and a compound of the composition MCl,NH_3Cl is formed.

We may further remark that in the series Mg, Zn, Cd, and Hg the capacity to form double salts of diverse composition increases with the atomic weight. Thus, according to Wells and Walden's observations (1893), the ratio $n : m$ for the type nMCl,$m$$RCl_2$ (M = K, Li, Na . . . R = Mg, Zn . . .) is for Mg, 1 : 1, and for Zn, 3 : 1, 2 : 1, and 1 : 1; for Cd, in addition, salts are known with the ratio 4 : 1, and for Hg, 3 : 1, 2 : 1, 1 : 1, 2 : 3, 1 : 2, and 1 : 5.

is sometimes, as in the alloy with Na or K, higher than that of the component metals, &c. Thus, for instance, if about 2½ per cent. of sodium is dissolved in mercury, a hard, crystalline amalgam is obtained, very friable and little changeable in air. It contains the compound $NaHg_5$ (Chap. XII., note 39). Water decomposes it, with the evolution of hydrogen, but more slowly than other sodium amalgams, and this action of water only shows that the bond between the sodium and the mercury is weak, just like the connection between mercury and many other elements—for instance, nitrogen. Mercury directly and easily dissolves potassium, sodium, zinc, cadmium, tin, gold, bismuth, lead, &c., and from such solutions or alloys it is in most cases easy to extract definite compounds; thus, for instance, the compounds of mercury and silver have the compositions $HgAg$ and Ag_2Hg_3. Objects made of copper when rubbed with mercury become covered with a white coating of that metal, which slowly forms an amalgam; silver acts in the same way, but more slowly, and platinum combines with mercury with still greater difficulty. This metal only forms an amalgam readily when in the form of a fine powder. If salts of platinum in solution are poured on to an amalgam of sodium, the latter element reduces the platinum, and the platinum separated is dissolved by the mercury. Almost all metals readily form amalgams if their solutions are decomposed by a galvanic current, where mercury forms the negative pole (cathode). In this way an amalgam may even be made with iron, although iron in mass does not dissolve in mercury. Some amalgams are found in nature—for instance, silver amalgams. Amalgams are used in considerable quantities in the arts. Thus the solubility of silver in mercury is taken advantage of for extracting that metal from the ore by means of amalgamation, and for silvering by fire. The same is the case with gold. Tin amalgam, which is incapable of crystallising and is obtained by dissolving tin in mercury, composes the brilliant coating of ordinary looking-glasses—silver is now preferred for this purpose (Chap. XXIV.) —which is made to adhere to the surface of the polished glass by simply pressing, by mechanical means, sheets of tin foil bathed in mercury on to the cleansed surface of the glass.[27]

---

[27] I consider it appropriate here to call attention to the want of an element (ekacadmium) between cadmium and mercury in the periodic system (Chap. XV.). But as in the ninth series there is not a single known element, it may be that this series is entirely composed of elements incapable of existing under present conditions, or it may be replaced by the rare metals (Chap. XVII.). However, until this is proved in one way or another, it may be concluded that the properties of ekacadmium will be between those of cadmium and mercury. This metal ought to have an atomic weight of about 155, to form an oxide EcO and a slightly stable oxide Ec_2O. Both these ought to be feeble bases,

easily forming double and basic salts. The volume of the oxide will be approximately 17·5, because the volume of cadmium oxide is about 16, and that of mercuric oxide 19. Therefore the density of the oxide will approach 171÷17·5=9·7. The metal ought to be easily fusible, oxidising when heated, of a grey colour, with a specific volume about 14 (cadmium=13. mercury=15), and, therefore, its specific gravity (155÷14) will be about 11. Such a metal is unknown. But in 1879 Dahl, in Norway, discovered in the island of Oterö, not far from Krageerö, in a vein of Iceland spar in a nickel mine, traces of a new metal which he called **norwegium,** and which presented a certain resemblance to eka-cadmium. I have not heard more about it, and possibly it is not a new element after all. A solution of the roasted mineral in acid was twice precipitated by sulphuretted hydrogen, and again ignited; the oxide obtained was easily reduced.

Amongst the metals accompanying zinc but not authentically separated, the **actinium** of Phipson (1881) might be mentioned if the information about it were more authentic and its name did not give the probability of its being confused with the actinium which possesses the radio-active properties mentioned in Chap. XXI. on Uranium.

CHAPTER XVII

BORON, ALUMINIUM, AND THE ANALOGOUS METALS OF THE THIRD GROUP

If the elements of small atomic weight which we have hitherto discussed be placed in order, it will be clearly seen that, judging by the formulæ of their higher compounds, one element is wanting between beryllium and carbon. For lithium, Li=7, gives LiX, beryllium, Be=9, forms BeX_2, and then comes carbon, C=12, giving CX_4. Evidently to complete the series we must look for an element forming RX_3, and having an atomic weight greater than 9 and less than 12. And such a one is **boron**; its atomic weight is 11, and its compounds are expressed by BX_3. Lithium and beryllium are metals; carbon has no metallic properties; boron appears in a free state in several forms which are intermediate between the metals and non-metals. Lithium gives an energetic caustic oxide and beryllium forms a very feeble base; hence one would expect to find that the oxide of boron, B_2O_3, has still more feeble basic properties and some acid properties, especially as CO_2 and N_2O_5, which follow B_2O_3 in their composition and in the periodic system, are acid oxides. And, indeed, the only known **oxide of boron** exhibits a feeble basic character, together with the properties of a feeble acid oxide. This is even seen from the fact that a solution of boron oxide reddens blue litmus and acts on turmeric paper as an alkali, and these reactions may be used for determining the presence of B_2O_3 in solutions. By themselves the alkali borates have an alkaline reaction, which clearly indicates the feeble acid character of boric acid. If they are mixed in solution with hydrochloric acid, boric acid is liberated, and if a piece of turmeric paper is immersed in this solution and then dried, the excess of hydrochloric acid volatilises, while the boric acid remains on the paper, and communicates a **brown coloration to the turmeric**, just like alkalies.

Boron trioxide or boric anhydride enters into the composition of many minerals, either in combination with bases or in small quantities as an isomorphous admixture, not replacing acids but bases, and most frequently alumina (Al_2O_3), for as a rule the amount of alumina present decreases as that of the boric anhydride increases. This substitution is explained by the similarity between the atomic composition of the oxides of aluminium (alumina) and boron. The subdivision of oxides into basic and acid can in no way be sharply defined, and here we meet with the most conclusive proof of the fact, for the oxides of boron and aluminium belong to the number of intermediate oxides, closely approaching the limit separating the basic from the acid oxides. Their type R_2O_3 is intermediate between those of the basic oxides, R_2O and RO, and those of the acid oxides, R_2O_5 and RO_3. If we turn our attention to the chlorides, we remark that lithium chloride is soluble in water, is not volatile, and is not decomposed by water; the chlorides of beryllium and magnesium are more volatile, and are still decomposed by water, although not completely; whilst the chlorides of boron and aluminium are still more volatile and are decomposed by water. Thus the positions of boron and aluminium in the series of the elements are clearly defined by their atomic weights, and show us that we must not expect any new and distinct functions in these elements.

Boron was originally known in the form of sodium borate, $Na_2B_4O_7,10H_2O$, or **borax**, or *tincal*, which was exported from Asia, where it is met with in solution in certain lakes of Thibet; it has also been discovered in California and Nevada, U.S.A.[1] Boric acid was afterwards found in sea water and in certain mineral springs.[2] Its

---

[1] Borax is obtained either directly from lakes, or by heating native calcium borate (see note 2) with sodium carbonate or else from the impure boric acid of Tuscany and sodium carbonate (carbonic anhydride is evolved). Borax gives supersaturated solutions with comparative ease (Gernez), and crystallises from them, both at the ordinary and higher temperatures, in octahedra, of the composition $Na_2B_4O_7,5H_2O$. Its sp. gr. is 1·81. But if the crystallisation proceeds in open vessels, then at temperatures below 56°, the ordinary prismatic crystallo-hydrate $B_4Na_2O_7$, $10H_2O$ is obtained. Its sp. gr. is 1·71, it effloresces in dry air at the ordinary temperature, and at 0° 100 parts of water dissolve about 3 parts of this crystallo-hydrate, at 50°, 27 parts and at 100°, 201 parts. Borax fuses when heated, loses its water, and gives an anhydrous salt, which at a red heat fuses into a mobile liquid and solidifies into a transparent amorphous *glass* (sp. gr. 2·37) which before hardening acquires the pasty condition peculiar to common molten glass. Molten borax dissolves many oxides and on solidifying acquires characteristic tints with the different oxides; thus oxide of cobalt gives a dark-blue glass, nickel a yellow, chromium a green, manganese an amethyst, uranium a bright yellow, &c. Owing to its fusibility and its property of dissolving oxides, borax is employed in soldering and brazing metals. Borax frequently enters into the composition of strass and fusible glasses, and, in general, many kinds of glass for special purposes, such as that used for making thermometers, &c., often contain the elements of borax.

[2] We may mention the following among the minerals which contain boron: calcium borate, $(CaO)_3(B_2O_3)_4(H_2O)_6$, found and extracted in Asia Minor, near Brusa; *boracite* (stassfurtite), $(MgO)_6(B_2O_3)_8,MgCl_2$, at Stassfurt, in large crystals of the regular system and also amorphous masses (specific gravity 2·95), used in the arts; *ereméeffite* (Damour), $AlBO_3$ or Al_2O_3,B_2O_3, found in the Adulchalonsk mountains in

presence may be discovered by means of the green coloration it communicates to the flame of alcohol, which is capable of dissolving free boric acid.[3] Many of the boron compounds employed in the arts are obtained from the impure boric acid extracted in Tuscany from the so-called fumaroles (*suffioni*). In these localities, which present the remains of volcanic action, steam mixed with nitrogen, hydrogen sulphide, small quantities of boric acid, ammonia, and other substances, issues from the earth.[3a] The boric acid partially volatilises with the steam, for if a solution of boric acid be boiled, the distillate will always contain a certain amount of this substance.[4]

---

colourless transparent prisms (specific gravity 3·28) resembling apatite; *datholite* $(CaO)_2(SiO_2)_2B_2O_3,H_2O$; and *ulksite,* or the boron-sodium carbonate, from which a large quantity of borax is now extracted in America (note 1). As much as 10 per cent. of boric anhydride sometimes enters into the composition of tourmaline and axinite.

[3] This green coloration is best seen by taking an alcoholic solution of volatile ethyl borate, which is easily obtained by the action of boron chloride on alcohol.

[3a] P. Chigeffsky showed in 1884 (at Geneva) that in the evaporation of saline solutions many salts are carried off by the vapour; for instance, if a solution of potash containing about 17–20 grams of K_2CO_3 per litre be boiled, about 5 milligrams of salt are carried off for every litre of water evaporated. With Li_2CO_3 the amount of salt carried over is infinitesimal, and with Na_2CO_3 it is half that given by K_2CO_3. The volatilisation of B_2O_3 under these circumstances is incomparably greater; for instance, when a solution containing 14 grams of B_2O_3 per litre is boiled, every litre of water evaporated carries over about 350 milligrams of B_2O_3. When Chigeffsky passed steam through a tube containing B_2O_3 at 400°, it carried away so much of this substance that the flame of a Bunsen's burner into which the steam was led gave a distinct green coloration; but when, instead of steam, air was passed through the tube there was no coloration whatever. By placing a tube with a cold surface in steam containing B_2O_3, Chigeffsky obtained a crystalline deposit of the hydrate $B(OH)_3$ on the surface of the tube. Besides this, he found that the amount of B_2O_3 carried over by steam increases with the temperature, and that crystals of $B(OH)_3$ placed in an atmosphere of steam (although perfectly still) volatilise, showing that this is not a matter of mechanical transfer, but is based on the capacity of B_2O_3 and $B(OH)_3$ to pass into a state of vapour in an atmosphere of steam.

[4] How it is that these vapours containing boric acid are formed in the interior of the earth is at present unknown. Dumas supposes that it depends on the presence of **boron sulphide,** B_2S_3 (others think boron nitride), at a certain depth in the earth. This substance may be artificially prepared by heating a mixture of boric acid and charcoal in a stream of carbon bisulphide vapour, or by the direct combination of boron and the vapour of sulphur at a white heat. The almost non-crystalline compound B_2S_3, sp. gr. 1·55, thus obtained is somewhat volatile, has an unpleasant smell, and is very easily decomposed by water, forming boric acid and hydrogen sulphide, $B_2S_3 + 3H_2O = B_2O_3 + 3H_2S$. It is supposed that a bed of boron sulphide lying at a certain depth below the surface of the earth comes into contact with sea water which has percolated through the upper strata, becomes very hot, and gives steam, hydrogen sulphide, and boric acid. The amount of boric anhydride in the vapours which escape from the Tuscan fumaroles and suffioni is very inconsiderable—less than one-tenth per cent.—so that the direct extraction of the acid would be very uneconomical; for this reason the heat contained in the discharged vapours is made use of for evaporating the water. This is done in the following manner: Reservoirs are constructed over the crevices evolving the vapours and the water of some neighbouring spring is passed into them. The vapours are caused to pass through these reservoirs, and in so doing they give up all their boric acid

If boric acid is introduced into an excess of a strong hot solution of sodium hydroxide, on slowly cooling, the salt $NaBO_2,4H_2O$ crystallises out. This salt contains an equivalent of Na_2O to one equivalent of B_2O_3. It might be termed a neutral salt did it not possess strongly alkaline reactions and split up easily into alkali and the more stable borax or biborate of sodium mentioned above, which contains $2B_2O_3$ to Na_2O.[5] This salt is prepared by the action of boric acid

---

to the water and heat it, so that after about twenty-four hours it even boils; in this way, however, only a very weak solution of boric acid is obtained. This solution is then passed into lower basins and again saturated by the vapours discharged from the earth, by which means a certain amount of the water is evaporated and a fresh quantity of

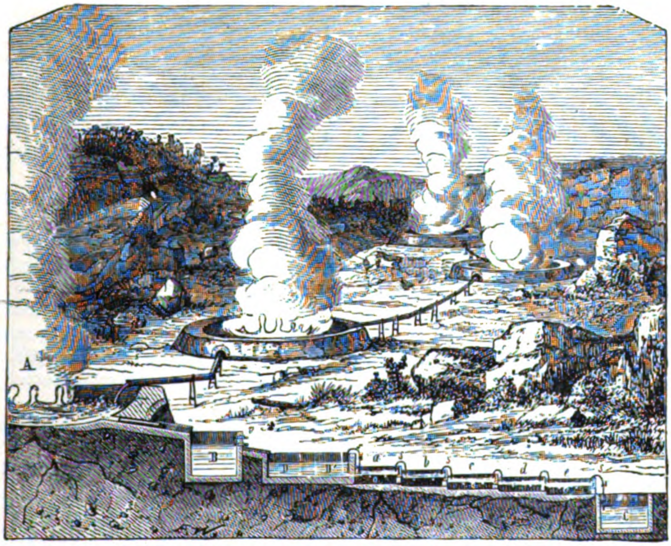


FIG. 91.—Extraction of boric acid from the fumaroles of Tuscany.

boric acid absorbed; the same process is repeated in other reservoirs until the water has collected a somewhat considerable amount of boric acid. The solution is drawn from the last reservoir, A, into settling vessels, B, D, and then into a series of vessels, *a*, *b*, *c*. In these vessels, which are made of lead, the solution is also evaporated by the vapours escaping from the earth, and attains a density of 10° to 11° Baumé.

[5] Metals, like Na, K, Li, give salts of the types MBO_2 or MH_2BO_3. A solution of borax, $Na_2B_4O_7$, has an alkaline reaction, decomposes ammonium salts with the liberation of ammonia (Bolley), absorbs carbonic anhydride, and dissolves iodine like an alkali (Georgiewics), and seems to be decomposed by water. Thus Rose showed that strong solutions of borax give a precipitate of silver borate with silver nitrate, whilst dilute solutions precipitate silver oxide, like an alkali. Georgiewics showed (1888) that all acids, acting on a mixture of solutions of potassium iodide and iodate, evolve iodine, but boric acid does not do this. With dilute solutions of sodium hydroxide Berthelot obtained a development of heat equal to 11½ thousand calories per equivalent of alkali (40 grams of sodium hydroxide) when the ratio was $Na_2O : 2B_2O_3$ (as in borax) and only

on a solution of sodium carbonate. Borax may be perfectly purified by crystallisation, the crystals usually containing $Na_2O + 2B_2O_3 + 10H_2O = Na_2B_4O_7,10H_2O$. If a saturated and hot solution of borax is mixed with strong hydrochloric acid, common salt and a normal crystalline hydrate of **boric acid** $B(OH)_3$, having the composition $B_2O_3,3H_2O$, are formed. The hydrate is only slightly (about 3 per cent.) soluble in water. This is the easiest method of obtaining boric acid. The water is easily expelled from this hydrate, one half being lost at 100° and the remainder on further heating, and the remaining B_2O_3 or boric anhydride fuses at 580° (according to Carnelley), forming at first a ductile (easily drawn out into threads) tenacious mass and then a colourless liquid solidifying to a transparent glass, which absorbs moisture from the atmosphere and then becomes cloudy.[6] Only the alkaline salts of boric acid are soluble in water, but all borates are soluble in acids, owing to their easy decomposability and the solubility of boric acid itself. Although **boric anhydride**, B_2O_3, absorbs $3H_2O$ from damp air, still in the presence of water it always [7] combines with

---

4 thousand calories when it was $Na_2O : B_2O_3$, from which he concludes that water powerfully decomposes those sodium borates in which there is more alkali than in borax. Laurent (1849) obtained a sodium compound, $Na_2O, 4B_2O_3,10H_2O$, containing twice as much boric anhydride as borax, by boiling a mixture of borax with an equivalent quantity of sal-ammoniac until the evolution of ammonia entirely ceased.

Hence it is evident that feeble acids are prone to form acid salts (that is, salts containing much acid oxide) as readily as feeble bases give basic salts. These relations become still clearer on an acquaintance with such feeble acids as silicic, molybdic, &c. This variety of the proportions in which bases are able to form salts recalls exactly the variety of the proportions in which water combines with crystallo-hydrates.

With respect to the feeble acid energy of boric anhydride I think it useful to add the following remarks. Carbonic anhydride is absorbed by a solution of borax, and displaces boric anhydride; but it is also displaced by it, not only on fusion, but also on solution, as the preparation of borax itself shows. Sulphuric anhydride is absorbed by boric acid, forming a compound $B(HSO_4)_3$, where HSO_4 is the radicle of sulphuric acid (D'Ally). With phosphoric acid, boric acid forms a stable compound, BPO_4, or B_2O_3,P_2O_5, undecomposable by water, as Gustavson and others have shown. With respect to tartaric acid, boric anhydride is able to play the same part as antimonious oxide. Mannitol, glycerol, and similar polyhydric alcohols also form particularly characteristic compounds with boric anhydride.

[6] Ditte determined the sp. gr.:—

	0°	12°	80°
B_2O_3	1·8766	1·8476	1·6988
$B(OH)_3$	1·5463	1·5172	1·3828
Solubility	1·95	2·92	16·82

The last line gives the solubility, in grams, of boric acid, $B(OH)_3$, per 100 c.c. of water, also according to the determinations of Ditte.

[7] It is evident that, in the presence of basic oxides, water competes with them, which fact in all probability determines both the amount of water in the salts of boric acid as well as their decomposition by an excess of water. In confirmation of the abovementioned competing action between water and bases, I think it useful to point out that the crystallo-hydrate of borax containing $5H_2O$ may be represented as $B(HO)_3$, or

a small quantity of bases. Fused boric anhydride forms a crystalline compound $(MgO)_3B_2O_3$ (Ebelmann) with magnesia of the same type as the hydrate, and even with soda it forms $(Na_2O)_3B_2O_3$ or Na_3BO_3 (Benedict). Generally, vitreous fluxes are formed by this means,[8] and these, when fused, recall ordinary aqueous solutions in many respects. Some of them crystallise on solidifying, and such have, like salts, a definite composition. The property of boric anhydride of forming higher grades of combination with basic oxides when fused explains the power of fused borax to dissolve metallic oxides, and the experiments of Ebelmann on the preparation of artificial crystals of the precious stones by means of boric anhydride. Boric anhydride is, although with difficulty, volatile at a high temperature, and therefore if it dissolves an oxide, it may be partially driven off from such a solution by prolonged and powerful ignition; in which case the oxide previously in solution separates out in a crystalline form, and frequently in the same form as that in which it occurs in nature; for example, crystals of alumina, which by itself fuses with difficulty, have been obtained in this manner. It dissolves in molten boric anhydride, and separates out in natural rhombohedric crystals. In this way Ebelmann also obtained *spinel*, a compound of magnesium and aluminium oxides which occurs in nature.[9]

---

rather as $B_2(OH)_6$, with the substitution of one atom of hydrogen by sodium, since $Na_2B_4O_7,5H_2O = 2B_2(OH)_5(ONa)$. The composition of the acid boric salts is very varied, as is seen from the fact that Reychler (1893) obtained $(Cs_2O),3B_2O_3$, $(Rb_2O),2B_2O_3$ (corresponding to borax) and $(Li_2O),B_2O_3$, and that Le Chatelier and Ditte obtained, for CaO, MgO, &c., $(RO)B_2O_3$, $(RO)_23B_2O_3$, $(RO)2B_2O_3$, $(RO)_2B_2O_3$, and even $(RO)_3B_2O_3$

[8] A glass can only be formed by those slightly volatile oxides corresponding with feeble acids, like silica, phosphoric and boric anhydrides, &c., which themselves give glassy masses, like quartz, glacial phosphoric acid, and boric anhydride. They are able, like aqueous solutions and like metallic alloys, either to solidify in an amorphous form or to yield (or even be wholly converted into) definite crystalline compounds. This view illustrates the position of solutions among other chemical compounds, and allows all alloys to be regarded from the point of view of the common laws of chemical reactions. I have therefore frequently recurred to it in this work, and have since the year 1850 introduced it into various provinces of chemistry.

[9] Although boric acid in aqueous solution proves to be exceedingly feeble and unenergetic, and to be easily displaced from its salts by other acids, yet in an anhydrous state, as anhydride, it exhibits the properties of an energetic acid oxide, and **displaces the anhydrides of other acids.** This of course does not mean that the acid then acquires new chemical properties, but depends only on the fact that the anhydrides of the majority of acids are much more volatile than boric anhydride, and therefore the salts of many acids—even of sulphuric acid—are decomposed when fused with boric anhydride.

By itself boric acid is used in the arts in small quantity, chiefly for the preservation of meat and fish (which must be afterwards well washed in water) and of milk, and for soaking the wicks of stearin candles. The latter application is based on the fact that the wicks, which are made of cotton twist, contain an ash which is infusible by itself, but which fuses when mixed with boric acid.

Free **boron** was obtained (1809) by Davy, Gay-Lussac, and Thénard when they obtained the metals of the alkalies, for when boric anhydride is fused with sodium it gives up its oxygen to the sodium, and free boron is liberated as an **amorphous** powder resembling charcoal.[10] It is of a brown colour, specific gravity 2·45 (Moissan), and when dry does not alter in the air at the ordinary temperature; but it burns when ignited to 700°, and in so doing combines not only with the oxygen of the air, but also with the nitrogen. However, the combustion is never complete, because the boric anhydride formed on the surface fuses and covers the remaining mass of the boron, and so preserves it from the action of the oxygen. Acids, even sulphuric (forming SO_2) and phosphoric (forming phosphorus), easily oxidise amorphous boron, especially when heated, converting it into boric acid. Alkalies have the same action on it, only in this case hydrogen is evolved. Boron decomposes steam at a red heat, also with evolution of hydrogen.

Amorphous boron, like charcoal, dissolves in certain molten metals. The property of fused **aluminium of dissolving boron** in considerable quantity is very striking; on cooling such a solution, the boron partially combined with the aluminium separates out in a crystalline form, and its properties are then exceedingly remarkable. The crystalline boron may be obtained by heating (to 1300°) the pulverulent boron with aluminium in a well-closed crucible, the access of air being prevented as far as possible. After cooling, crystals are observed

---

[10] **Amorphous boron** is prepared by mixing 100 parts of powdered boric anhydride with 50 parts of sodium in small lumps; this mixture is thrown into a powerfully heated cast-iron crucible, covered with a layer of ignited salt, and the crucible covered. Reaction proceeds rapidly; the mass is stirred with an iron rod, and poured directly into water containing hydrochloric acid. The action is naturally accompanied by the formation of sodium borate, which is dissolved, together with the salt, by the water, whilst the boron settles at the bottom of the vessel as an insoluble powder. It is washed in water, and dried at the ordinary temperature. Magnesium, and even charcoal and phosphorus, are also able to reduce boron from its oxide. Boron, in the form of an amorphous powder, very easily passes through filter-paper, remains suspended in water, and colours it brown, so that it appears to be soluble in water. Sulphur precipitated from solutions shows the same (colloidal) property. When borax is fused with magnesium powder, it gives a brown pulverulent compound of boron and magnesium, Mg_2B (Winkler, 1890); but when a mixture of 1 part of magnesium and 3 parts of B_2O_3 is heated to redness (Moissan 1892), it yields amorphous boron in the form of a chestnut-coloured powder, which, after being washed with water, hydrochloric and hydrofluoric acids, is again fused with B_2O_3 in an atmosphere of hydrogen in order to prevent the access of the nitrogen of the air, which is easily absorbed by incandescent amorphous boron.

Sabatier (1891) considers that a certain amount of gaseous hydride of boron is evolved in the action of hydrochloric acid upon the alloys of magnesium and boron, because the gas disengaged burns with a green flame. Still, the existence of hydride of boron cannot be regarded as certain. However, according to Winkler, a solid compound of boron and hydrogen exists, although it has not yet been obtained in a pure state.

Under the action of the heat of the electric furnace, boron forms with carbon a *carbide*, BC, as was shown by Mühlhäuser and Moissan in 1893.

on the surface of the aluminium, and may easily be separated by dissolving the latter in hydrochloric acid, which does not act on the crystals. The specific gravity of the latter is 2·68; they are partially transparent, but for the most part are coloured dark brown; they contain about 4 per cent. of carbon and up to 7 per cent. of aluminium, so that they cannot be considered as pure boron. Nevertheless, the properties of this **crystalline** substance, which was obtained by Wöhler and Deville, are very remarkable. It most closely resembles the **diamond in its properties**; in fact, these crystals have the lustre and high refracting power proper to the diamond only, whilst their hardness competes with that of the diamond. Their powder polishes even the diamond, and like the diamond scratches the sapphire and corundum. Crystalline boron is much more stable with respect to chemical reagents than the amorphous variety, and just as it resembles the diamond, so amorphous boron, on the other hand, distinctly recalls certain of the properties of charcoal; thus a certain resemblance exists between boron and carbon in a free state, which is further justified by the proximity of their positions in the periodic systems.

Among the other compounds of boron, those with nitrogen and the halogens are the most remarkable. As already mentioned above, amorphous boron combines directly with **nitrogen** at a red heat. If it is heated in a glass tube in a stream of nitric oxide, perfect combustion takes place: $5B+3NO=B_2O_3+3BN$. If the residue is treated with nitric acid, the boric anhydride dissolves, whilst the boron nitride remains[11] as an extremely light white powder, which is sometimes partially crystalline and greasy to the touch, like talc. It is infusible and remains unchanged even at the melting-point of nickel. In general, it is remarkable for its great stability with respect to chemical reagents. Nitric and hydrochloric acids, as well as alkaline solutions, and hydrogen and chlorine at a red heat, have no action on it. When fused with potash, it evolves ammonia, and when ignited in steam it also yields ammonia: $2BN+3H_2O=B_2O_3+2NH_3$.[12]

---

[11] At first boron nitride was obtained by heating boric acid with potassium cyanide or other cyanogen compounds. It may be more simply prepared by heating anhydrous borax with potassium ferrocyanide, or by heating borax with ammonium chloride. For this purpose one part of borax is intimately mixed with two parts of dry ammonium chloride, and the mixture heated in a platinum crucible. A porous mass is formed, which, after crushing and treating with water and hydrochloric acid, leaves boron nitride.

[12] When fused with potassium carbonate it forms potassium cyanate, $BN+K_2CO_3=KBO_2+KCNO$. All this shows that boron nitride is a nitrile of boric acid, $BO(OH)+NH_3-2H_2O=BN$. The same is expressed by saying that boron nitride is a compound of the type of the boron compounds BX_3, with the substitution of X_3 by nitrogen, as the trivalent radicle of ammonia, NH_3. *Boron phosphide*, BP, corresponding with BN, was prepared by Besson and Moissan (1891). The action of phosphorus on boron iodide, BI_3,

No less remarkable is the compound of boron with fluorine—**boron fluoride**, BF_3. It is produced in many instances when a compound of boron and one of fluorine are brought together.[13] The most convenient method of preparing it is by heating a mixture of calcium fluoride with boric anhydride and sulphuric acid: $3CaF_2 + B_2O_3 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 2BF_3$.[14] It is a colourless liquefiable *gas* (the liquid boils at −100°), which on coming into contact with damp air forms white fumes owing to its combining with water. One volume of water dissolves as much as 1,050 volumes of this gas (Bazaroff), forming a liquid which disengages boron fluoride when heated, and distils over unaltered. Boron fluoride chars organic matter, owing to its taking up the water from it, and in this respect it acts like sulphuric acid. The behaviour of boron fluoride with water must be understood as a reversible reaction, since with water it yields hydrofluoric and boric acids, whilst they, acting on one another, re-form boron fluoride and water. A state of equilibrium is set up between these four substances (and between two reversible reactions) which is distinctly dependent on the mass of the water.[14a] When boron fluoride is in great excess, the equilibrated system, which is capable of distilling over (sp. gr. of the liquid, 1·77), has a composition $BF_3,2H_2O$, (or $B_2O_3,H_2O,6HF$). It has also its corresponding salts.[15] It is a caustic liquid, having the properties of a powerful acid; but it does not act on glass, which shows

---

yields PBI_2, and this, when heated to 500° in hydrogen, gives BP, which with fused potassium hydroxide gives rise to PH_3.

[13] Boron fluoride is frequently evolved on heating certain compounds occurring in nature containing both boron and fluorine. If calcium fluoride is heated with boric anhydride, calcium borate and boron and fluorine are formed, and the latter, as a gas, is volatilised: $2B_2O_3 + 3CaF_2 = 2BF_3 + Ca_3B_2O_6$. The calcium borate, however, retains a certain amount of calcium fluoride.

[14] In order to avoid the formation of silicon fluoride the decomposition should not be carried on in glass vessels, which contain silica, but in a lead or platinum vessel. Boron fluoride by itself does not corrode glass, but the hydrofluoric acid liberated in the reaction may bring a part of the silica into reaction. Boron fluoride should be collected over mercury, since water acts on it, as we shall see later.

[14a] It appears to me that from this point of view it is possible to understand the apparently contradictory results of different investigators, especially those of Gay-Lussac (and Thénard), Davy, Berzelius, and Bazaroff. From the form in which the reaction of BF_3 on water is given here, it is evident that the act of solution in water is accompanied by complex chemical transformations, and I think that this example again proves the justness of those observations upon the nature of solutions given in Chap. I.

[15] They are called fluoborates. They may be prepared directly from fluorides and borates. Such compounds of halogens with oxygen salts are known in nature (for instance, apatite and boracite), and may be artificially prepared. The composition of the fluoborates—for example, $K_4BF_3O_2$—may be expressed as that of a double salt, BO(OK),3KF. Although an excess of water decomposes them (Bazaroff), this does not prove that they do not exist as such, for many double salts are decomposed by water.

that there is no free hydrofluoric acid present. Under the action of water this system changes, with the formation of boric acid and hydrofluoboric acid (HBF_4), according to the equation: $4BF_3H_4O_2 = 3HBF_4 + BH_3O_3 + 5H_2O$.[16] This hydrofluoboric acid has its corresponding salts—for instance, KBF_4. On evaporating the aqueous solution of the free acid it decomposes, with the evolution of hydrofluoric acid, and a stable system is again obtained: $2HBF_4 + 5H_2O = B_2F_6H_{10}O_5 + 2HF$. The resultant solution (containing $2BF_3,5H_2O$, sp. gr. 1·58), which is identical with that formed by the evaporation of a solution of boric acid with hydrofluoric acid, again only contains a compound of boron fluoride with water. Probably there are various other possible and more or less stable states of equilibrium and definite compounds of boron fluoride, hydrofluoric acid, and water.

Nothing of this kind occurs with boron chloride, because hydrochloric acid does not act on boric acid. However, at 400° amorphous boron burns in chlorine, and at 410° forms **boron chloride**, BCl_3, obtained as a gas which, in a freezing mixture, condenses into a liquid boiling at 17°, and gives up its excess of chlorine, if there be any, to mercury. The specific gravity of this liquid is 1·42 at 6°. Boron chloride may also be directly obtained from boric anhydride by the simultaneous action of charcoal and chlorine at a high temperature; $B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO$. It is also obtained by the action of phosphoric chloride on boric anhydride in a closed tube at 200°. It is completely decomposed by water, like the chloranhydride of an acid, boric acid being formed; hence it fumes in the air: $2BCl_3 + 6H_2O = 2BH_3O_3 + 6HCl$. Boron forms with bromine a similar compound, BBr_3, having the specific gravity 2·64 at 6° and boiling at 90°. The vapour densities of the fluoride, chloride, and bromide of boron show that they contain three atoms of the halogen in the molecule—that is, that boron is a trivalent element forming BX_3.[16a]

As in the first group lithium is followed by sodium, giving a more basic oxide, so in the second group beryllium is followed by magnesium,

---

[16] Fluoboric acid contains boron fluoride and water; hydrofluoboric acid, boron fluoride, and hydrofluoric acid. It is evident that on the one side the competition between water and hydrofluoric acid, and, on the other hand, their power to combine, are among the forces which act here. From the fact that hydroborofluoric acid, HBF_4, can only exist in an aqueous solution, it must be assumed that it forms a somewhat stable system only in the presence of $8H_2O$.

[16a] Iodide of boron, BI_3, was obtained by Moissan (1891), by heating a mixture of the vapours of HI and BCl_3 in a tube, or by the action of iodine vapour (at 750°) or HI upon amorphous boron. BI_3 is a solid substance which dissolves in benzene and CS_2, reacts with water, melts at 43°, boils at 210°, has a density 3·3 at 50°, and partially decomposes in the light. Besson (1891) obtained $BIBr_2$ (boiling at 125°) and BI_2Br (boiling at 180°) by heating 300°–400°) a mixture of the vapours of HI and BBr_3, and he showed also that NH_3 combines with BBr_3 and BI_3 in various proportions.

and so also in the third group there is, besides the lightest element, boron, whose basic character is scarcely defined, **aluminium**, Al=27, the oxide of which, alumina, has somewhat distinct basic properties, not so powerful as in magnesium oxide, but more distinct than in boric anhydride. Of the elements of the third group, aluminium is the most widely distributed in nature; it will be sufficient to mention that it enters into the composition of clay to demonstrate the universal distribution of aluminium in the earth's crust. Aluminium is so named from its being the metal of alums (*alumen*). **Clay**, which is so widely distributed and familiar to everybody, is the insoluble residue obtained after the action of water containing carbonic acid on many rocks, and especially on the felspars contained in some of them. Felspar is a compound containing potash or soda, alumina, and silica. The primary rocks, like granite, contain many similar compounds (see Chap. XVIII.: Felspars). Felspar is acted on by water containing carbonic acid, all the alkalies (potash and soda) and a portion of the silica passing into the water as substances which are soluble and carried away by it, whilst the alumina and silica left from the felspar remain on the spot where the solution has taken place. This is the original method of the formation of clay in its primary deposits among rocks along the crevices of which the atmospheric water has permeated. Such primary deposits often contain a white pure clay, termed **kaolin** or **porcelain clay**. But such clay is a rarity, because the conditions for its formation are seldom met with. The water, while acting chemically on rocks, at the same time destroys them *mechanically*, and carries off the finely divided residues of disintegration with it. Clay is most easily subjected to this mechanical action of water, because it is composed of grains of exceedingly small size and void of any visible crystalline structure, which readily remain suspended in water. The cloudy water of running mountain streams generally contains suspended particles of clay, formed by the above-described chemical and mechanical action of the water on the minerals contained in the mountain rocks. Together with these minute particles of clay the water carries away the coarser components on which it is not able to act—for example, splinters of rock, grains of mica, quartz, &c. They were originally held together by those minerals which form clay. When the water acts on these binding minerals, a sandy mass is formed which water bears away. The cloudy water in which the particles of clay and sand are held in suspension carries them to, and deposits them at, the estuaries of rivers, lakes, seas, and oceans. The coarser particles are first deposited and form sand and similar disintegrated rocky matter, whilst the clay, owing to its finely divided state, is carried on further, and is only deposited in the still parts of the rivers, lakes, &c. Such disintegration of rocks and separation of clay from sand has been gradually going on during the millions of years of the earth's existence, and is now proceeding, and has been the cause of the formation of immense deposits of sandstone and clay. Beds of clay may have been transferred by currents and streams from one locality to another, so that we must distinguish between primary and secondary deposits of clay. In some places these beds of clay have, owing to long exposure under water, and partially owing to the action of heat, undergone compression, and have formed the rocky masses known as clay slates and schists, which sometimes form entire mountains. Roofing slates belong to this class of rocks.

From what has been said above it will be evident that these deposits can never consist of a chemically pure and homogeneous substance, but will contain all kinds of extraneous, insoluble, finely divided matter, and especially sand—that is, fragments of rock, chiefly quartz (SiO_2). It is, however, possible to considerably purify clay from these impurities, owing to the fact that they are the result of mechanical disintegration, whilst the clay has been formed as a residue of the chemical alteration of rocky matter, and therefore its particles are incomparably more minute than the particles of sand and other rock fragments mixed with it. This difference in the size of the grains causes the clay to remain longer in suspension than the coarser grains of sand, when shaken up in water. If clay be shaken up in water, and especially if it be previously boiled in it, and if after the first portion has settled the cloudy water be decanted, it will give a deposit of a very much purer clay than the original. This method is employed for purifying kaolin designed for the manufacture of the best kinds of china, earthenware, &c. A similar method is also employed in the investigation of earths for determining the **composition of soils**, which are chiefly composed of a mixture of sand, clay, limestone, and mould. The limestone is soluble in dilute acids, but neither the clay nor sand passes into solution by this means, and therefore the limestone is easily separated in the investigation of soils. The clay is separated from the sand by a mechanical method similar to that described above, and termed *levigation*.[17]

---

[17] The process of **levigation** is based on the difference in the diameters of the particles of clay and sand. In density these particles differ but little from each other, and a stream of water of a certain velocity can only carry away the particles of a certain diameter, whilst the particles of a larger diameter cannot be borne away by it. This is due to the resistance to falling offered by the water. This resistance to substances moving in it increases with the velocity, and therefore a substance falling into water will only move with an increasing velocity until its weight equals the resistance offered by

By treating clay with strong sulphuric acid, which dissolves the alumina in it, and then (by means of an alkaline carbonate) dissolving the

the water, and then the velocity will be uniform. And as the weight of the minute particles of clay is small, the maximum velocity attained by them in falling is also small. (A detailed account of the theory of bodies falling in liquids, and of the experiments bearing on this subject, may be found in my work, *Concerning the Resistance of Liquids and Aeronautics*, 1880.) The minute particles of clay remain suspended longer in water, and take longer to fall to the bottom. Heavy particles, although of small dimensions, fall more quickly, and are borne away by water with greater difficulty than the lighter. In this way gold and other heavy ores are washed free from sand and clay, and the coarser portions and heavier particles are left behind. A current of water of a certain velocity cannot carry away with it particles of more than a definite diameter and density, but by increasing the velocity of the current a point may be arrived at when it will bear away larger particles. A description of apparatus for the observation of phenomena of this kind is given by Schöne in his memoir in the *Transactions of the Moscow Society of Natural Sciences* for 1867. In order to be able to vary accurately the velocity of the current of water, a cylinder is employed in which the earth to be experimented on is placed, and water is introduced through the conical bottom of the cylinder. The rate at which the water rises in the cylinder will vary according to the quantity of water flowing per unit of time into the vessel, and consequently particles of various sizes will be carried away by the water flowing over the upper edges of the vessel. Schöne showed by direct experiment that a current of water having a velocity of 0·1 mm. per second will carry away particles of earth having a diameter of not more than 0·0075 mm., that is, only the most minute; with a velocity $v=0{\cdot}2$ mm. per second, particles having a diameter $d=0{\cdot}011$ mm. are carried away; with $v=0{\cdot}3$ mm., $d=0{\cdot}0146$ mm.; with $v=0{\cdot}4$ mm., $d=0{\cdot}017$ mm.; with $v=0{\cdot}5$ mm., $d=0{\cdot}02$ mm.; with $v=1$ mm., $d=0{\cdot}03$ mm.; with $v=4$ mm., $d=0{\cdot}07$ mm.; with $v=10$ mm., $d=0{\cdot}137$ mm.; with $v=12$ mm., $d=0{\cdot}15$ mm.; and therefore if the current does not exceed one of these velocities, it will only carry or wash away particles having a diameter less than that indicated. The sand and other particles mixed with the clay will then remain in the vessel. The very minute particles obtained after levigation are all considered as clay, although not only clay but other rock residue may also exist in it as very fine particles. However, this is very seldom the case, and the fine mud separated from all clays has practically the same composition as the purest kinds of kaolin.

The relation between the amounts of clay and sand in soils used for the cultivation of plants is very important, because a soil rich in clay is denser and heavier and shrinks up under the action of heat, and does not readily yield to the plough in very dry or wet weather, whilst a rich soil in sand is friable and crumbling, easily parts with its moisture, and dries rapidly, but is comparatively easily worked. Neither crumbling sand nor pure clay can be regarded as a good cultivating soil. The difference in the amounts of clay and sand in a soil has also a purely chemical signification. Sand is easily permeated by the air, because its particles are not closely packed together. Hence the chemical change of manures proceeds very easily in sandy soils. But on the other hand such soils do not retain the nutritious principles contained in the manure, nor the water necessary for the nourishment of plants by means of their roots, and are much injured by drought. Solutions of nutritious substances, containing salts of potassium, phosphoric acid, &c., when passed through sand only leave a portion moistening the surface of its particles. The sand has only to be washed with pure water, and all the adhering films of solution are washed away. It is not so with clay. If the above solutions be passed through a layer of clay, the retention of the nutritive substances of these solutions will be very marked; this is partly because of the very large surface which the minute particles of clay expose. The nutritive elements dissolved in water are retained by the particles of clay in a peculiar manner—that is, the absorptive power of clay is very great compared with that of sand—and this has a great significance in the economy of nature (Chap. XIII.). It is silica which was combined with the alumina in the clay (but not that occurring in the form of sand, &c., which is hardly dissolved by carbonate of soda solution at all even on boiling), we may form an idea of the proportion between the component parts of a clay; and by igniting it at a high temperature we may determine the amount of water held in it. In the purer sorts of clay dried at 100° (sp. gr. of pure kaolin is about 2·5) this proportion is about $2SiO_2 : 2H_2O : Al_2O_3$. In this case the conversion of felspar into kaolin is expressed by the equation:

$$\underset{\text{Felspar}}{K_2O,Al_2O_3,6SiO_2} = \underset{\text{Kaolin}}{Al_2O_3,2SiO_2} + K_2O,4SiO_2;$$

the compound $K_2O,4SiO_2$ passes into solution.

---

evident that for cultivation the most convenient soils in every respect will be those containing a definite mixture of clay and sand, and indeed the most fertile soils have such a composition. The study of fertile soils, which is so important for a knowledge of the natural conditions for the application of fertilisers, belongs, strictly speaking, to the province of agriculture. In Russia the first foundation of scientific fertilisation has been laid by Prof. V. V. Dokuchaeff. As an example only, we shall give the composition of four soils: (1) The black earth of the Simbirsk government; (2) a clay soil from the Smolensk government; (3) a more sandy soil from the Moscow government; and (4) a peaty soil from near St. Petersburg. These analyses were made in the laboratory of the St. Petersburg University about 1860, in connection with experiments on fertilisation (conducted by me) by the Imperial Free Economical Society. Ten thousand grams of air-dried soil contain the following quantities (in grams) of substances capable of dissolving in acids, and of serving for the nourishments of plants.

	(1)	(2)	(3)	(4)
Na_2O	11	5	4	4
K_2O	58	10	7	5
MgO	92	33	19	7
CaO	134	17	14	11
P_2O_5	7	1	7	3
N	44	11	13	16
S	13	7	7	6
Fe_2O_3	341	155	111	46

By chemical and mechanical analysis, the chief component parts per 100 parts of the four air-dried soils were found to be:—

Clay	46	29	12	10
Sand	40	67	86	84
Organic matter	3·7	1·7	0·6	4·1
Hygroscopic water	6·8	1·8	0·8	1·9
Weight of a litre in grams	1150	1270	1350	960

The black earth excels the other soils in many respects, but naturally its stores are also exhausted by cultivation if nothing is returned to it in the form of fertilisers; and the improvement of a soil (for instance, by the addition of marl or peat, and by drainage and watering), and its fertilisation, if carried on in conformity with its composition and with the properties of the plants to be cultivated, are capable of rendering not only every soil fit for cultivation, but also of improving its value, so that in the course of time whole countries (like Holland) may clearly improve their agricultural position, whilst under the ordinary *régime* of continued exhaustion of the soil, entire regions (as, for instance, many parts of Central Asia) may be rendered unfit for any agriculture.

But as a rule clays contain from 45 to 60 per cent. of silica, from 20 to 30 of alumina, and about 12 of water; and it cannot be supposed that clays are always homogeneous, because they are an aggregation of residues (of silico-aluminous compounds) which are unacted on by water. Nevertheless, clays always contain a hydrated compound of alumina and silica, which is able to give up the alumina contained by it as a base to strong sulphuric acid, forming aluminium sulphate, which is soluble in water. After this treatment the silica remains, and is soluble in a solution of an alkaline carbonate.[18]

Clay is the source from which alumina, Al_2O_3, and the majority of the compounds of aluminium are prepared. Among these compounds the most important are the alums—that is, the double sulphates of potassium (and allied metals) and aluminium, $AlK(SO_4)_2,12H_2O$. When clay is treated with sulphuric acid diluted with a certain amount of water, aluminium sulphate, $Al_2(SO_4)_3$, is formed; and if potassium carbonate or sulphate is added to this solution, a double salt or alum is obtained in solution. The alums crystallise easily, and are prepared on a very large manufacturing scale owing to their being employed in the process of dyeing. Alums are soluble in water, and, on the addition of ammonia to their solutions, they give **hydrated**

---

[18] Everyone knows that a mixture of clay and water is endowed with the property of taking a given form when subjected to a moderate pressure. This plasticity of clay renders it an invaluable material for practical purposes. From clay are moulded and manufactured a variety of objects, beginning with the common brick and ending with the most delicate china works of art. This **plasticity of clay** increases with its purity. When articles made of clay are dried, the well-known hard mass is obtained; but water washes it away, and, furthermore, the cohesion of its particles is not sufficiently great for it to resist the impression of blows, shocks, &c. If such an article be subjected to the action of heat, its volume first decreases, then it begins to lose water, and shrinks still further. On the other hand, a great coherence of particles is obtained, and thus burnt clay has the hardness of stone. Pure clay, however, shrinks so considerably when burnt that the form given to it is destroyed and cracks easily form; such vessels are also porous, so that they will not hold water. The addition of sand—that is, silica in fine particles—or of chamotte—that is, already burnt and crushed clay—renders the mass much more dense and incapable of cracking in the furnace. Nevertheless, such clay articles (bricks, earthenware vessels, &c.) are still porous to liquids after being burnt, because the clay in the furnace is only baked and does not fuse. In order to obtain articles impervious to water the clay must either be mixed with substances which form a glassy mass in the furnace, permeating the clay and filling up its pores, or else only the surface of the article is covered with such a glassy fusible substance. In the first case the purest kinds of clay give what is known as china, in the second case porcelain or 'faïence,' majolica, &c. Thus, for instance, by covering the surface of clay articles with a layer of the oxides of lead and tin, the well-known white glaze of tiles, &c., is obtained, because the oxides of these metals give a white gloss when fused with silica and clay. In the preparation of china, fluor spar and finely ground silica are mixed up into the clay; these ingredients give a mass which is infusible but softens in the furnace, so that all the particles of the clay cohere in this softened mass, which hardens on cooling. A glaze composed of glassy substances, which only fuse at a high temperature, is also applied to the surface of china articles.

alumina or **aluminium hydroxide**, as a white gelatinous precipitate, which is insoluble in water but easily soluble in acids, even when dilute, and in aqueous soda or potash. The solubility of alumina in acids indicates the basic character of the oxide, and its solubility in alkalies and its power of forming compounds with them show the weakness of this basic character. However, the feeblest acids, even carbonic acid, take up the alkali from such a solution, and the alumina then separates out in a precipitate as the hydroxide. It must also be remembered as characteristic of the salt-forming properties of alumina that it does not combine with such feeble acids as carbonic, sulphurous, or hypochlorous, &c.—that is, its compounds with these acids are decomposed by water. It is also important to observe that the hydroxide is not soluble in aqueous ammonia.

Alumina, Al_2O_3—that is, the anhydrous aluminium oxide—is met with in nature, sometimes in a somewhat pure state, having crystallised in transparent crystals, which are often coloured by impurities (chromic, cobaltic, and ferric compounds). Such are the ruby and sapphire, the former red and the latter blue. They have a specific gravity 4·0, are distinguished by their very great hardness, which is second only to that of the diamond, and they represent the purest form of alumina. They are found in Ceylon and other islands of the Indian Archipelago, embedded in a rock matrix.[18a] **Corundum** is the same crystallised anhydrous alumina coloured brown by a trace of oxide of iron. A very much larger portion of this impurity occurs in **emery**, which is found in crystalline masses in Asia Minor and in the State of Massachusetts, and owing to its extreme hardness is employed for polishing stones and metals. In this anhydrous and crystalline state, aluminium oxide is a substance which very powerfully resists the action of reagents, and is insoluble both in solutions of the alkalies

---

[18a] Frémy (1890) obtained transparent rubies, which crystallised in rhombohedra, and resembled natural rubies in their hardness, colour, size, and other properties. He heated together a mixture of anhydrous alumina, containing more or less caustic potash, with barium fluoride and bichromate of potassium. The latter is added to give the ruby its colour, and is taken in small quantity (not more than 4 parts by weight to 100 parts of alumina). The mixture was put into a clay crucible, and heated (for from 100 hours to 8 days) in a reverberatory furnace at a temperature approaching 1500°. At the end of the experiment the crucible was found to contain a crystalline mass, and the walls were covered with crystals of the ruby of a beautiful rose colour. It was found that the access of moist air was indispensable for the reaction. According to Frémy, the formation of the ruby may be here explained by the formation of fluoride of aluminium which under the action of the moist air at the high temperature of the furnace gives the ruby and hydrofluoric acid gas. Alumina easily fuses and sometimes gives crystals like rubies in the heat of the electric furnace or at the temperature produced by the combustion of Al at the expense of Fe_2O_3 (Chap. III., note 42), i.e., about 3000°.

and in strong acids. It is only capable of passing into solution after being fused with alkalies and bisulphate of potassium, $KHSO_4$.[19] Alumina may be obtained in this refractory form if the hydroxide be ignited and then fused in the oxyhydrogen flame.[20] Alumina also occurs in nature in combination with water—as, for instance, in the rather rare minerals, hydrargillite (sp. gr. 2·3), $Al_2O_3,3H_2O=2Al(HO)_3$, and diaspore, $Al_2O_3,H_2O=2AlO(HO)$ (sp. gr. 3·4). A less pure hydrate, mixed with ferric oxide, sometimes occurs in masses (at Baux in the South of France) and is termed **bauxite**; it contains $Al_2O_3,2H_2O=Al_2O(HO)_4$ (sp. gr. 2·6). When bauxite is ignited with sodium carbonate, carbonic anhydride is liberated and the alumina then combines with the sodium oxide, forming a saline aluminate of the oxides of aluminium and sodium. This is taken advantage of in practice for the preparation of pure alumina compounds on a large scale, for bauxite is found in large masses (in the South of France, in Austria, and in Carolina in North America), and the resultant compound of alumina and sodium is soluble in water and does not contain ferric oxide. This solution when subjected to the action of carbonic anhydride gives a precipitate of aluminium hydroxide,[21] which with acids forms aluminium salts. If

---

[19] The effects of purely mechanical subdivision on the solubility of alumina are evident from the fact that native anhydrous alumina, when converted into an exceedingly fine powder by means of levigation, dissolves in a mixture of strong sulphuric acid and a small quantity of water, especially when heated in a closed tube at 200°, or when fused with acid sulphate of potassium (see Chap. XIII., note 9).

[20] When alumina, moistened with a solution of cobalt salt, is ignited, it forms a blue mass called Thénard's salt. This coloration is taken advantage of not only in the arts, but also for distinguishing alumina from other earthy substances resembling it.

[21] The treatment of bauxite is carried on on a large scale, chiefly in order to obtain alumina from alkaline solutions, free from ferric oxide, because in dyeing it is necessary to have salts of aluminium which do not contain iron. But this end, it would seem, may also be obtained by igniting alumina containing ferric oxide in a stream of chlorine mixed with hydrocarbon vapours, as ferric chloride then volatilises. K. Bayer observed that in the treatment of bauxite with soda, about 4 molecules of sodium hydroxide pass into solution to 1 molecule of alumina, and that on agitating this solution (especially in the presence of some already precipitated aluminium hydroxide), about two-thirds of the alumina is precipitated, so that only 1 molecule of alumina to 12 molecules of sodium hydroxide remains in solution. This solution is evaporated directly, and used again. He therefore treats bauxite directly with a solution of NaHO at 170° in a closed boiler, and on cooling adds hydrated alumina to the resultant solution. The greater part of the dissolved alumina then precipitates on this hydrated alumina, and the solution is used over again. The hydroxide which separates from the alkaline solution has the composition $Al(OH)_3$. These properties bear a great resemblance to those of boric acid. It is found that the relation between the sodium hydroxide and alumina varies with the mass of water.

If lime is added to a solution of alumina in alkali (sodium aluminate), calcium aluminate is precipitated, from which acids first extract the lime, leaving aluminium hydroxide, which is then easily soluble in acids (Loewig). When sodium aluminate is mixed with a solution of sodium bicarbonate, a double carbonate of the alkali and aluminium is precipitated, which is easily soluble in acids.

aqueous ammonia be added to a solution of aluminium sulphate a gelatinous precipitate is formed, which at first remains suspended in the liquid and then on settling forms a gelatinous mass, which itself indicates the **colloidal property of aluminium hydroxide.** The following points are characteristic of this colloidal state: (1) in an anhydrous state such a colloidal substance is insoluble in water, as alumina is; (2) in the hydrated state, it is gelatinous and insoluble in water; and (3) it is also capable of existing in solutions, from which it separates out in a non-crystalline state, forming a substance resembling glue. These different states of colloids were distinguished by Graham, who gave them the following very characteristic names. He called the gelatinous form of the hydrate **hydrogel,** i.e., a gelatinous hydrate, and the soluble form of the aqueous compound, **hydrosol,** from the Latin for a soluble hydrate. Alumina readily and frequently assumes these states. The gelatinous hydrate of alumina is its hydrogel. Like all similar hydrogels, it shows not the faintest sign of crystallisation; it is apt to vary in many of its properties with the amount of water it contains, and loses its water on ignition, leaving a white powder of the anhydrous oxide. The hydrogel of alumina is soluble both in acids and alkalies. It may also be obtained by the evaporation of its solutions in such feebly energetic acids as volatile acetic acid. These properties are very frequently made use of in the arts, and especially in **the processes of dyeing,** because the hydrogel of alumina in precipitating attracts a number of colouring matters from their solutions, the precipitate being thus coloured by the dyes attracted.[22] The preparation of fixed dyes

---

[22] These coloured precipitates of alumina are termed *lakes*, and are employed in dyeing tissues and in the formation of various pigments—such as pastels, oil colours, &c. Thus, if organic colouring matters, such as logwood, madder, &c., are added to a solution of any aluminium salt, and then an alkali added, so that alumina may be precipitated, these pigments, which are by themselves soluble in water, will come down with the precipitate. This shows that alumina is able to combine with the colouring matter, and that this compound is not decomposed by water. The dyes then become insoluble in water. If a dye be mixed with starch paste and aluminium acetate, and then, by means of engraved blocks having a design in relief, we transfer this mixture to a fabric which is then heated, the aluminium acetate will leave the hydrogel of alumina which binds the colouring matter, and water will no longer be able to wash the pigment from the material —that is, a so-called 'fixed' dye is obtained. In the case of dyeing a fabric a uniform tint, it is first soaked in a solution of aluminium acetate and then dried, by which means the acetic acid is driven off, while the hydrogel of alumina adheres to the fibres of the material. If the latter be then passed through a solution of a dye in water, the former will be attracted to the portions covered with alumina, and will closely adhere to them. If certain parts of the material be protected by the application of an acid, such as tartaric, $C_4H_6O_6$, oxalic, citric, &c. (these acids being non-volatile), the alumina will be dissolved in those parts, and the pigment will not adhere, so that after washing, a white design will be obtained on those parts which have been so protected.

In dye-works the aluminium acetate is generally obtained in solution by taking a solution of alum, and mixing it with a solution of lead acetate. In this case lead and the employment of aluminous compounds (mordants) in the processes of dyeing are founded on this fact.[23] When precipitated upon the fibres of tissues (calicoes, linens, &c.) the aluminium hydroxide renders them impermeable to water; this may be taken advantage of for the preparation of waterproof tissues.

The **hydrosol** of alumina—i.e., the soluble aluminium hydroxide—is more difficult to obtain.[24] In order to obtain this soluble variety of

---

sulphate is precipitated and aluminium acetate remains in solution, together with either acetate or sulphate of potassium, according to the amount of acetate of lead first taken. The complete decomposition will be as follows: $KAl(SO_4)_2 + 2Pb(C_2H_3O_2)_2 = KC_2H_3O_2 + Al(C_2H_3O_2)_3 + 2PbSO_4$, or the less complete decomposition, $2KAl(SO_4)_2 + 3Pb(C_2H_3O_2)_2 = 2Al(C_2H_3O_2)_3 + K_2SO_4 + 3PbSO_4$. If the resultant solution of aluminium acetate is evaporated or further boiled, the acetic acid passes off and the hydrogel of alumina remains.

As the salt of potassium obtained in the solution passes away with the water used for washing, and the salt of lead precipitated has no practical use, this method for the preparation of aluminium acetate cannot be considered economical; it is retained in the process of dyeing mainly because both the salts employed, alum and sugar of lead, easily crystallise, and it is easy to judge of their degree of purity in this form. Indeed, it is very important to employ pure reagents in dyeing, because if impurity is present—such as a small quantity of an iron compound—the tint of the dye changes; thus madders give a red colour with alumina, but if oxide of iron is present the red changes into a violet tint. The aluminium hydroxide is soluble in alkalies, whilst ferric oxide is not. Therefore **sodium aluminate** —that is, the dissolved compound of alumina and caustic soda—obtained, as already described, from bauxite, is sometimes employed in dyeing. Every aluminium salt gives a solution containing sodium aluminate free from iron, when it is mixed with excess of caustic soda. This solution, when mixed with a solution of ammonium chloride, gives a precipitate of the hydrogel of alumina: $Al(OH)_3 + 3NaHO + 3NH_4Cl = Al(OH)_3 + 3NaCl + 3NH_4OH$. There was originally free soda, and on the addition of sal-ammoniac there is free ammonia, which does not dissolve alumina, so that the hydrogel of the latter is precipitated.

[23] Another direct method for the preparation of pure aluminium compounds consists in the treatment of **cryolite** containing aluminium fluoride, together with sodium fluoride, $AlNa_3F_6$. This mineral is exported from Greenland, and is also found in the Urals. It is crushed and heated in reverberatory furnaces with lime, and the resultant mass treated with water; sodium aluminate is then obtained in solution, and calcium fluoride in the precipitate: $AlNa_3F_6 + 3CaO = 3CaF_2 + AlNa_3O_3$.

[24] Crum first prepared a solution of basic acetate of alumina—that is, a salt containing as large an excess as possible of aluminium hydroxide with the smallest possible quantity of acetic acid. The solution must be dilute—that is, must not contain more than one part of alumina per 200 of water—and if this solution is heated in a closed vessel (so that the acetic acid cannot evaporate) to the boiling-point of water, for one and a half to two days, the solution, which apparently remains unaltered, loses its original astringent taste, proper to solutions of all the salts of alumina, and has instead the purely acid taste of vinegar. The solution then no longer contains the salt, but acetic acid and the hydrosol of alumina in an uncombined state; they may be isolated from each other by evaporating the acetic acid in shallow vessels at the ordinary temperature. If the solution be diluted with water, it may even be heated to drive off the acetic acid, and with a thin layer of liquid the alumina does not separate as a precipitate. When the acid vapours cease to come off there remains a solution of the hydrosol of alumina, which is tasteless and has no action on litmus paper. When concentrated, this solution acquires a more and more gluey consistency, and when completely evaporated over a water-bath it leaves a non-crystalline glue-like hydrate, the composition of which is $Al_2H_4O_5$

alumina, Graham took a solution of its hydrogel in hydrochloric acid—that is, a solution of aluminium chloride, which is able to dissolve a still further quantity of the hydrogel of alumina, forming a basic salt having probably the composition, $Al(HO)Cl_2$ or $Al(HO)_2Cl$. When such a solution, considerably diluted with water, is subjected to dialysis—that is, to diffusion through a membrane[25]—the hydrochloric acid diffuses through the membrane and leaves the alumina in the form of hydrosol. The resultant solution, even when only containing two or three per cent. of alumina, passes into the hydrogel state with such facility that it is sufficient to transfer it from one vessel to another which has not been previously washed with water, for the entire mass to solidify into a jelly. But a solution containing not more than one-half per cent. of alumina may even be boiled without coagulating; however, after the lapse of several days, this solution will of its own accord yield the hydrogel of alumina.[25a]

With respect to alumina as a base, it is very important to observe that it is not only capable of combining with other bases,[26] but does not give salts with feeble volatile acids (like carbonic and hypochlorous); it forms salts which are easily decomposed by water, especially when heated,[27] as well as double and basic

---

$=Al_2O_3,2H_2O$. The smallest quantity of alkalies, and of many acids and salts, will convert the hydrosol into the hydrogel of alumina—that is, convert the aluminium hydroxide from a soluble into an insoluble form, or, as it is said, cause the hydrate to coagulate or gelatinise. Many such colloidal solutions are known (Chap. I., note 57).

[25] In a dialyser, Chap. I., note 18.

[25a] The different states in which the hydrates of alumina occur and are prepared resemble similar varieties of the hydrates of the oxides of iron and chromium, of molybdic and tungstic acids, as well as of phosphoric and silicic acids, of many sulphides, proteid substances, &c. We shall therefore have occasion to recur to this subject in the further course of this work.

The most remarkable peculiarity of Graham's solution is that it solidifies on litmus paper, and leaves a blue ring on it, which shows the alkaline—that is, basic—character of the alumina in such a solution. If in the dialysis the basic hydrochloric acid salt is replaced by a similar acetic acid salt, a hydrosol of alumina is obtained which does not act upon litmus (note 24).

[26] Compounds of alumina with bases (aluminates, see note 21) are sometimes met with in nature. Such are spinel, $MgO,Al_2O_3=MgAl_2O_4$; chrysoberyl, $BeAl_2O_4$, and others. Magnetic oxide of iron, $FeO,Fe_2O_3=Fe_3O_4$, and compounds like it, belong to the same class. Here we evidently have a case of combination 'by analogy,' as in solutions and alloys, accompanied by the formation of strictly definite saline compounds, and such instances form a clear transition from so-called solutions and certain mixtures to the type of true salts.

[27] Not only aluminium acetate (note 24), but also every other aluminium salt with a volatile acid, parts with its acid on heating in aqueous solution—that is, is decomposed by water, and forms either basic salts or a hydrate of alumina. By dissolving aluminium hydroxide in nitric acid we may easily obtain a well-crystallising **aluminium nitrate**, $Al(NO_3)_3,9H_2O$, which fuses at 73° without decomposing (Ordway), gives a basic salt, $2Al_2O_3,6HNO_3$ at 100°, and at 140° leaves the aluminium hydroxide perfectly

salts,[28] so that it **forms a clear example of a feeble base.**[29] To these characteristics of alumina we must add that it gives not only compounds of the type AlX_3, but also of the polymeric type Al_2X_6, even when X is a simple univalent haloid like chlorine. Deville and Troost showed (1857) that the vapour density of aluminium chloride (at about 400°) is 9·37 with respect to air—that is, nearly 135 with respect to hydrogen, and therefore the formula of its molecule at about 400° is expressed by Al_2Cl_6, but at higher temperatures (1000° and 1300°) its density corresponds to $AlCl_3$,[30] although in the case of boron, arsenic,

---

free from the elements of nitric acid. But the solutions of this salt, like those of the acetate, are also able to yield aluminium hydroxide. From all this it is evident that we must suppose that the solutions of this and similar salts contain an equilibrated dissociated system, consisting of the salt, the acid, and the base, and their compounds with water, as well as partly the molecules of water itself.

[28] As an example of native basic salts we may cite **alunite**, or alum-stone (sp. gr. 2·6), which sometimes occurs in crystals, but more frequently in fibrous masses. It has been found in masses in the Caucasus (at Zaglik, distant forty versts from Elizabetpol), and at Tolfa, near Rome. Its composition is $K_2O,3Al_2O_3,4SO_3,6H_2O$ (alunite contains $9H_2O$). It is soluble in water but is not decomposed by it, but after being slightly ignited it gives up alum to it. It may be artificially prepared by heating a mixture of alum with aluminium sulphate in a closed tube at 230°.

[29] As the colloidal properties are particularly sharply developed in those oxides (Al_2O_3, SiO_2, MoO_3, SnO_2, &c.) which show (like water also) the properties of feeble bases and feeble acids, there is probably some causal reason for this coincidence, all the more so since among organic substances—gelatins, albumins, &c.—the representatives of the colloids also have the property of feebly combining with bases and acids.

[30] Since Deville's experiments the question of the density of aluminium chloride has been frequently re-investigated. The subject has more especially occupied the attention of Nilson, Pettersson, Friedel and Crafts, and V. Meyer and his collaborators. In general, it has been found that at low temperatures (up to 440°) the density is constant, and indicates a molecule Al_2Cl_6; whilst depolymerisation probably takes place at higher temperatures, and the molecule $AlCl_3$ is obtained. Along with this there has been, and still is, a difference of opinion as to the vapour density of aluminium ethyl and methyl—whether, for instance, $Al(CH_3)_3$ or $Al_2(CH_3)_6$ expresses the molecule of the latter. The interest of these researches is intimately connected with the question of the valency of aluminium, if we hold to the opinion that elements in their various compounds have a constant and strictly definite valency. In this case the formula $AlCl_3$ or $Al(CH_3)_3$ would show that Al is trivalent, and that consequently the compounds of aluminium are $Al(OH)_3$, AlO_3Al, and, in general, AlX_3. But if the molecule is Al_2Cl_6, it is—for the followers of the doctrine of the invariable valency of the elements—incompatible with the idea of the trivalency of aluminium, and they assume it to be quadrivalent like carbon, likening Al_2Cl_6 to ethane $C_2H_6 = CH_3CH_3$, although this does not explain why Al does not form $AlCl_4$, or, in general, AlX_4. In this work another supposition is introduced; according to this, although aluminium, as an element of group III., gives compounds of the type AlX_3, this does not exclude the possibility of these molecules combining with others, and consequently with *each other*—that is, forming Al_2X_6; just as the molecules of univalent elements exist either as H_2, Cl_2, &c., or as Na, and the molecules of bivalent elements either as Zn, or as S_2, or even S_6. In the first place it must be recognised that the limiting form does not exhaust all power of combination, it only exhausts the capacity of the element for combining with X's; but the saturated substance may afterwards combine with *whole molecules*; a fact best proved by the capacity of substances to form crystalline compounds with water,

and antimony, which give oxides R_2O_3 of the same type as Al_2O_3, the chlorine compounds always form non-polymeric molecules, BCl_3, $AsCl_3$, $SbCl_3$.[31] This duplication (polymerisation) of the form AlX_3 is probably connected with the facility with which the salts of aluminium combine with other salts to form double salts, and with aluminium hydroxide itself to form basic salts.

Aluminium sulphate $Al_2(SO_4)_3$, which is obtained by treating clay or the hydrates of alumina with sulphuric acid, crystallises in the cold with $27H_2O$, or at the ordinary temperature in pearly crystals, which are greasy to the touch and contain $16H_2O$.[32] Its solutions act like sulphuric acid—for instance, they evolve hydrogen with zinc, forming

---

ammonia, &c. But in some substances this faculty for further combinations is less developed (for instance, in carbon tetrachloride, CCl_4), whilst in others it is more so. AlX_3 combines with many other molecules. Now if a limiting form, which does not combine with new X's, nevertheless combines with other whole molecules, it will naturally in some instances combine with itself, will polymerise. In this manner the mind clearly grasps the idea that the same forces which cause S_2 to unite itself to Cl_2, or C_2H_4 to Cl_2, &c., also unite molecules of a similar kind together; thus **polymerisation** ceases to be an isolated fragmentary phenomenon, and chemical combinations 'by analogy' acquire a particular and important interest. In conformity with these views the following proposition may be made concerning the compounds of aluminium. They are of the type AlX_3 in the limit, like BX_3, but those limiting forms are still able to combine to form AlX_3,RZ, and at low temperatures aluminium chloride is a compound of this kind—i.e. $(AlX_3)_2$. In boron, for example, in BCl_3, this tendency to form further compounds is less developed. Hence boron chloride appears as BCl_3, and not as $(BCl_3)_2$. Polymerisation is not only possible when a substance has not attained the limit (although it is more probable then), but also when the limiting form has been reached, if only the latter has the faculty of combining with other whole molecules. We may therefore conclude that aluminium, like boron, is trivalent in the same sense that lithium and sodium are univalent, magnesium bivalent, and carbon tetravalent. In a word, there is no reason to consider that aluminium is capable of forming compounds AlX_4, and in that way to explain the existence of the molecule Al_2Cl_6. Furthermore, there are many reasons for thinking that AlF_3, Al_2O_3, and other empirical formulæ do not express the molecular weights of these compounds, but that they are much higher: Al_nF_{3n}, $Al_{2n}O_{3n}$. Since I introduced this view in the seventies of the past century convincing proofs of the truth of the above statements, and of the independent existence of AlX_3 in a state of vapour have been obtained, for Combes (1889) has determined the vapour density of the volatile aluminium acetonyl-acetonate $Al(C_5H_7O_2)_3$ (which melts at 193°, boils at 315°, and distils without a trace of decomposition), and has found that it exactly corresponds to the above molecular composition. On the other hand, Louise and Roux (1889) by employing the method of 'freezing-point depression' of solutions (Chap. I., note 49) found that the molecules $Al_2(C_2H_5)_6$ and $Al_2(C_5H_{11})_6$, &c., correspond to the type Al_2X_6. Thus it may now be accepted that the molecular composition of the compounds of aluminium in their simplest form is AlX_3, but that they may polymerise and give Al_2X_6 or, in general, Al_nX_{3n}.

[31] In the case of gallium, as a close analogue of aluminium, Lecoq de Boisbaudran (1880) showed that the molecule of gallium chloride probably consists of Ga_2Cl_6 at low temperatures and high pressures, and that it dissociates into $GaCl_3$ at high temperatures and low pressures. The molecule of indium chloride seems to exist only in the simplest form, $InCl_3$.

[32] The pure salt ($16H_2O$) is not hygroscopic. In the presence of impurities the amount of water increases to $18H_2O$, and the salt becomes hygroscopic.

basic salts, which are sometimes met with in nature (*aluminite*, $Al_2O_3,SO_3,9H_2O$, and others)—and may be obtained by the decomposition of normal salts and by the direct solution of the hydroxide in normal salts: these exhibit a varying composition, $(Al_2O_3)_n(SO_3)_m(H_2O)_q$, where m/n is less than 3. Aluminium sulphate is prepared (pure from the hydrate obtained from bauxite, note 21) in large quantities for dyeing purposes (instead of alums) as a mordant and for the preparation of **alums** —the ordinary crystalline alum has the composition $KAl(SO_4)_2, 12H_2O$, and ammonium alums (which leave a residue of alumina when ignited) in which the potassium is replaced by ammonium (NH_4). Alums are used in large quantities, because they crystallise so easily. In this respect the alums formed by potassium and ammonium are equally convenient to purify, because they present a considerable difference in their solubility at the ordinary and higher temperatures. If the crystallisation is conducted rapidly, the salt separates in minute crystals, but if slowly deposited, especially in large masses, as in factories, then crystals several centimetres long are sometimes obtained.[33]

Aluminium chloride, Al_2Cl_6, is obtained, like other similar chlorides (for instance $MgCl_2$), either directly from chlorine and the metal, or by heating to redness an intimate mixture of the amorphous anhydrous oxide and charcoal in a stream of dry chlorine.[33a] A sublimate is

---

[33] The sodium alums are very much more soluble, and crystallise with greater difficulty, and are therefore less easily freed from impurities; at 0°, 100 parts of water dissolve 3 parts; at 30°, 22 parts; at 70°, 90 parts; and at 100°, 357 parts of potassium alum. The solubility of ammonium alum is slightly less. The specific gravity of potassium alum is 1·74, that of ammonium alum 1·63, and that of sodium alum 1·60. Alums easily part with their water of crystallisation; thus potash alum partially effloresces when exposed to the air, and loses 9 mol. H_2O under the receiver of an air-pump. At 100°, dry air passed over alums takes up nearly all their water. As we have already mentioned (Chap. XV.), the law of isomorphous substitutions exhibits itself more clearly in the alums than in any other salts, and all alums not only contain the same amount of water of crystallisation, $MR(SO_4)_2,12H_2O$ (where $M = K, NH_4, Na$; $R = Al, Fe, Cr$), and appear in crystals whose planes are inclined at equal angles, but they also give every possible kind of isomorphous mixture. The aluminium in them is easily replaced by iron, chromium, indium, and sometimes by other metals, while the potassium may be substituted by sodium, rubidium, ammonium, and thallium, and the sulphuric acid may be replaced by selenic and chromic acids. The common form of crystals of alums is octahedral, but if this solution contains a certain small excess of alumina above the ratio $2Al(OH_3)$ to K_2SO_4, and not more sulphuric acid than $3H_2SO_4$ to $2Al(OH)_3$, then it easily forms combinations of the cube and octahedron, and these alums are called 'cubic' alums. They are valued by the dyer because they can contain no iron in solution, for oxide of iron is precipitated before alumina, and if the latter be in excess there can be no oxide of iron present. These alums were long exported from Italy, where they were prepared from alunite (note 28). The potassium alums melt at about 92°, the ammonium alums at 95°, and the sodium alums at about 66°.

[33a] It is also formed by the action of hydrochloric acid upon metallic aluminium (Nilson and Pettersson), by heating alumina in a mixture of the vapours of naphthalene

obtained because the chloride is very volatile.[34] It forms a crystalline readily fusible mass, which deliquesces in the air and dissolves easily in water, with the evolution of a large amount of heat.[34a] On evaporating this solution, hydrochloric acid and aluminium hydroxide are liberated. But if the solution is heated in a closed tube, with an excess of hydrochloric acid, then, on cooling, crystals of $AlCl_3,6H_2O$ are obtained—that is, aluminium chloride both combines with water and is decomposed by it. And the faculty of the type AlX_3 for combining with other molecules is seen in the compounds of $AlCl_3$ with many other chlorine compounds. Thus, for example, a mixture of aluminium chloride with sulphur tetrachloride gives Al_2Cl_6,SCl_4, under the action of chlorine, whilst with phosphorus pentachloride it forms $AlCl_3,PCl_5$. The compounds $AlCl_3,NOCl$, $AlCl_3,POCl_3$, $AlCl_3,3NH_3$, $AlCl_3,KCl$, $AlCl_3,NaCl$ are also known.[35] The compound of aluminium and sodium chlorides,

---

and HCl (Faure, 1889), and by the action of dry HCl upon an alloy of 14 per cent. or more of Al with copper (Mobery).

[34] Aluminium chloride fuses at 178°, boils at 183° (pressure 755 mm., at 168° under a pressure of 250 mm., and at 213° under 2,278 mm.), according to Friedel and Crafts, so that it boils immediately after fusion. According to Seubert and Pallard (1892) Al_2Cl_6 fuses at 193°. Aluminium bromide fuses at about 92°, and the iodide at 185° according to Weber and at 125° according to Deville and Troost.

All these halogen compounds of aluminium are soluble in water. **Aluminium fluoride**, AlF_3 (Al_nF_{3n}), is insoluble in water; however, a solution is formed by dissolving alumina in hydrofluoric acid with an excess of acid. This solution probably contains the hydrosol of alumina or a compound of AlF and HF. When the solution is evaporated crystals of Al_2F_6,HF,H_2O are obtained which are insoluble in water. If this solution is saturated with a still larger amount of alumina, it deposits crystals having the composition, $Al_2F_6,7H_2O$, when evaporated. Perhaps the soluble form consists of AlF_3 and the insoluble one of a polymeride, Al_2F_6. All these compounds, when ignited, leave insoluble anhydrous aluminium fluoride. It forms colourless rhombohedra, which are non-volatile, of sp. gr. 3·1, and are decomposed by steam into alumina and hydrofluoric acid. The acid solution apparently contains a compound which has its corresponding salts; by the addition of a solution of potassium fluoride, a gelatinous precipitate of AlK_3F_6 is obtained. A similar compound occurs in nature—namely, $AlNa_3F_6$, or **cryolite**, sp. gr. 3·0.

[34a] In this respect aluminium chloride resembles the chlor-anhydrides of the acids, and probably in the aqueous solution the elements of the hydrochloric acid are already separated, at least partially, from the aluminium hydroxide. The solution may also be obtained by the action of aluminium hydroxide on hydrochloric acid.

[35] Here we see an example in confirmation of what has been said in note 30—i.e., the action of the molecule $AlCl_3$. We shall cite still another instance confirming the power of alumina to enter into complex combinations. Alumina, moistened with a solution of calcium chloride, gives, when ignited, an anhydrous crystalline substance (tetrahedral), which is soluble in acids, and has the composition $(Al_2O_3)_6(CaO)_{10}CaCl_2$. Even clay forms a similar stony substance which might be of practical use.

Among the most complex compounds of aluminium, **ultramarine**, or **lapis lazuli**, must be mentioned. It occurs in nature near Lake Baikal, in crystals, some colourless and others of various tints—green, blue, and violet. When heated it becomes dull and acquires a very brilliant blue colour. In this form it is used for ornaments (like malachite), and as a brilliant blue pigment. At the present time ultramarine is prepared artificially in large quantities as a paint, and this process is one of the most important

$AlNaCl_4$, is very fusible and much more stable in the air than aluminium chloride itself. It seems to be of the same type as the alums. This compound, $AlNaCl_4$, was for a long time employed in the extraction of metallic aluminium, as we shall presently proceed to describe. Aluminium bromide, which is obtained by the direct combination of metallic aluminium with bromine, closely resembles the chloride; it melts at 90°, volatilises at 270°. Aluminium iodide is obtained by heating iodine with finely divided aluminium in a closed tube; it is so easily decomposed by oxygen that its vapour even explodes when mixed with it.[36]

Metallic aluminium was first prepared by Wöhler in 1822 as a grey powder by the action of potassium on aluminium chloride. He afterwards (in 1845) obtained it as a white compact metal, unoxidisable in the air, and only slowly attacked by acids. Owing to the abundant and widespread occurrence of compounds of aluminium, many efforts have been made in investigating in detail the methods for the extraction of this metal. These efforts were brought to a successful issue (1845) by Sainte-Claire Deville, who is also renowned for his doctrine of dissociation. Experiments on a large scale have proved that metallic aluminium, although possessed of great lightness, strength, and durability, is not so generally suitable for technical purposes as was at first thought. Nitric and many other acids (especially organic), indeed, do not act on it, but the alkalies, dilute solutions of NH_3 and its salts, and even

---

conquests of science; for the blue tint of ultramarine has been the object of many scientific researches, which have culminated in the manufacture of this natural substance. The most characteristic property of ultramarine is that when placed in sulphuric acid it evolves hydrogen sulphide and becomes colourless. This shows that the blue colour of ultramarine is due to the presence of sulphides. If clay be heated in a furnace with sodium sulphate and charcoal (forming sodium sulphide) without access of air, a white mass is obtained, which becomes green when heated in the air, and when treated with water leaves a colourless substance known as 'white ultramarine.' When ignited in the air it absorbs oxygen and turns blue. The coloration is ascribed to the presence of metallic sulphides or polysulphides; but it is most probable that silicon sulphide, or its oxysulphide, SiOS, is present. At all events the sulphides play an important part, but the problem is not yet quite settled. The formula $Na_8Al_6Si_6O_{24}S$ is ascribed to white ultramarine. The green probably contains more sulphur, and the blue a still larger quantity. The last is supposed to have the composition $Na_8Al_6Si_6O_{24}S_3$. It is more probable (according to Guckelberger, 1882) that the composition of the blue form varies between $Si_{18}Al_{18}Na_{20}S_6O_{71}$ and $Si_{18}Al_{12}Na_{20}S_6O_{69}$. The latter may be expressed as $(Al_2O_3)_6(SiO_2)_{18}(Na_2O)_{10}S_6O_5$, which would indicate the presence of insufficiently oxidised sulphur in ultramarine.

[36] At the ordinary temperature aluminium does not decompose water, but if a small quantity of iodine, or of hydriodic acid and iodine, or of aluminium iodide and iodine, is added to the water, then hydrogen is abundantly evolved. It is evident that here the reaction proceeds owing to the temporary formation of AlI_3, and that this substance, with water, gives aluminium hydroxide and hydriodic acid, which, with aluminium, evolves hydrogen and re-forms AlI_3. Aluminium probably belongs to those metals having a greater affinity for oxygen than for the halogens (note 36b).

moist table salt, humidity, &c.,[36a] tarnish it, and hence objects made of aluminium suffer at the surfaces and alter, and the metal cannot, as was hoped, replace the precious metals, from which it differs in its extreme lightness. But the alloys made with aluminium (especially with copper, for example, aluminium bronze) are very valuable in their properties and applications.

Neither charcoal nor zinc will reduce the oxygen compounds of aluminium; even sodium and potassium do not act on alumina. Moreover, metallic aluminium, like magnesium, is able to reduce even the metals of the alkalies from their oxygen compounds. This is connected with the fact that the atom of oxygen evolves more heat in combining with Al (and Mg) than it does in combining with other metals; whilst, on the other hand, chlorine (and the other halogens) evolves more heat in combining with the metals of the alkalies.[36b]

The Deville method for the preparation of metallic aluminium is based on the decomposition of the above-mentioned compound of sodium and

---

[36a] As an example we may mention that if mercury comes into contact with metallic aluminium, and especially if it is rubbed upon the surface of aluminium moistened with a dilute acid, the Al becomes rapidly oxidised (Al_2O_3 being formed). The oxidation is accompanied by a very curious appearance, as it were, of wood (or fur) formed by threads of oxide of aluminium growing upon the metal. This was first pointed out by Cass in 1870, and subsequently by A. Sokoleff in 1892. This interesting and curious phenomenon leads to the formation of alumina. It does not proceed in an atmosphere of nitrogen, but takes place in a few minutes in ordinary air.

I think it necessary, however, to add that according to Lubbert and Rascher's researches (1891), wine, coffee, milk, oil, urine, earth, &c., have no more action upon aluminium vessels than upon copper, tin, and other similar articles. In the course of four months ordinary vinegar dissolved 0·35 grm. of Al per sq. centimetre, whilst a 5 per cent. solution of common salt dissolved about 0·05 grm. of aluminium. Ditte (1890) showed that Al is acted upon by nitric and sulphuric acids, although only slowly (owing to the formation of a layer of gas, as in Chap. XVI., note 10), and that the reaction proceeds much more rapidly *in vacuo* or in the presence of oxidising agents. Al is even oxidised by water on the surface, but the thin coating of alumina formed prevents further action. In the course of twelve hours nitric acid of sp. gr. 1·383 dissolved at 17° about 20 grms. of aluminium (containing only a small amount of Si, $1-\frac{1}{2}$ per cent.) from a sq. metre of surface (Le Rouart, 1891). A solution of NaCl produces oxidation: $Al_2 + 6NaCl + 3H_2O = Al_2Cl_6 + 3Na_2O + 3H_2$, and then: $Al_2Cl_6 + 3Na_2O = Al_2O_3 + 6NaCl$, so that the salt is renewed. Göttig (1896) showed that the action of a dilute solution of NH_3 on Al leads to the formation of an ammoniacal compound of the hydrate of alumina with the evolution of hydrogen, and that the presence of ammoniacal salts facilitates the action.

[36b] In addition to the data given in Chaps. XI., XIII., and in Chap. XV., note 19, the following are the amounts of heat in thousands of units evolved in the formation of the oxides and chlorides from the metals taken in gram-atomic quantities:

$$Na_2O\ 100;\ MgO\ 140^*;\ \tfrac{1}{3}\,Al_2O_3\ 120^*;\ \tfrac{1}{3}\,Fe_2O_3\ 63^*;$$
$$Na_2Cl_2\ 195;\ MgCl_2\ 151;\ \tfrac{1}{3}\,Al_2Cl_6\ 107;\ \tfrac{1}{3}\,Fe_2Cl_6\ 64.$$

The asterisks following the oxides of Mg, Al, and Fe call attention to the fact that the existing data refer to the formation of the hydrates of these metals, from which the heats of formation of the anhydrous oxides are only assumed, because the heats of hydration (for example, $MgO + H_2O$) have not yet been determined.

aluminium chlorides by metallic sodium. The compound is obtained by passing the vapour of aluminium chloride (evolved from a mixture of alumina, extracted from bauxite or cryolite, with charcoal ignited in a stream of chlorine) over red-hot salt, when the compound $AlNaCl_4$ is itself volatilised, and may in this manner be obtained pure. A mixture of this compound with salt and fluor spar, or with cryolite, is heated with a certain excess of sodium, cut into small lumps. On a large scale this operation is carried on in special furnaces with a small access of air and at a high temperature: $NaAlCl_4+3Na=4NaCl+Al$. Deville's method, which in the sixties of the nineteenth century gave the first large quantities of aluminium and the possibility of testing its applications in the arts, was complicated and expensive, and did not give metal sufficiently pure for many purposes, for instance, for replacing copper in electric conductors. Therefore when the dynamo was perfected in the eighties, many processes (Héroult, 1887, Borchers, Grabau, &c.) appeared for the preparation of aluminium by electrolysis at the high temperatures of the electric furnace. Bunsen (1854) and Deville (1854) had already obtained aluminium by electrolysis.

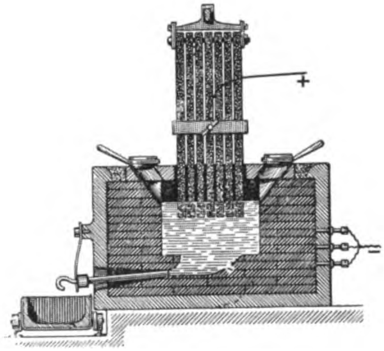


FIG. 92.—Héroult's electric furnace for preparing alloys of aluminium.

Since the close of the eighties the metallurgy of aluminium has taken a new direction, based upon the action of an electric current upon cryolite at a high temperature,[37] and the solution of oxide of aluminium (obtained from bauxite or in the form of corundum) in it; under these conditions metallic aluminium is reduced at the negative pole (cathode) in a sufficiently pure state, and, if the cathode be copper, forms alloys with it. Such are Hall's and Cowles's (both in the United States) and the Neuhausen process (where the current is obtained from a dynamo worked by the Falls of the Rhine at Schaffhausen). As an example, we shall describe (in the words of Prof. D. P. Konovalloff, who became acquainted with this process at the Chicago Exhibition) Hall's process as applied near Pittsburg, where it gives about 1,500 kilos of Al a day.

---

[37] Cryolite under the action of the current at about 1000° gives off the vapour of Na which reduces the Al, but it recombines with the liberated fluorine and again passes into the fused mass, which is able to dissolve alumina and so give a further quantity of Al. The alumina is either added from time to time or absorbed from the lining of the furnace.

An iron box (about 1 metre long and ½ metre wide), provided with a well-rammed-down charcoal lining, is charged with a mixture of cryolite and Al_2O_3 (from bauxite), over which salt is strewn, and a current of 5,000 ampères at 20 volts is passed through the mixture. The anode is composed of a carbon cylinder (about 9 cm. in diameter), while the charcoal lining forms the cathode. When the temperature inside the box is raised to a red heat by the current, the mixture fuses and the Al_2O_3 begins to decompose. The Al liberated collects at the bottom of the box, whilst the oxygen evolved burns the charcoal anode. When the decomposition is at an end, and the resistance of the mass increases, a fresh quantity of Al_2O_3 is added, and this is continued until the amount of impurities accumulated in the furnace and passing into the metal becomes too great.[37a]

Aluminium has a white colour slightly resembling that of tin—that is, it is greyer than silver and has the slightly dull lustre of tin, but, compared with tin and pure silver, aluminium is very hard. Its density is 2·67—that is, it is nearly four times as light as silver and three times as light as copper. It melts at an incipient red heat (600°), and in so doing is but slightly oxidised. At the ordinary temperature it does not alter in the air, and in a compact mass it burns with great difficulty at a white heat, but in thin sheets, into which it may be rolled, or as a very fine wire, it burns with a brilliant white light, since it forms an infusible and non-volatile oxide with the evolution of about 350,000 units of heat for Al_2O_3 (102 grms.). Aluminium itself is non-volatile at a furnace heat. These properties render it a very good reducing agent, and N. N. Beketoff showed that it reduces the oxides of the alkali metals (Chap. XIII., note 42a). Aluminium reduces iron, chromium, and similar metals from their oxides with still greater facility, and the reaction, owing to the comparatively small specific heat (and small amount) of the resulting substances, is accompanied by a powerful rise of temperature, sufficient not only to fuse the iron and oxide of aluminium,

---

[37a] The cost of working this process can be brought as low as tenpence per lb., or about two shillings per kilo. In England, Castner, prior to the introduction of the electric method, obtained Al by taking a mixture of 1,200 parts of the double salt $NaAlCl_4$, 600 parts of cryolite, and 350 parts of Na, and obtained about 120 parts of Al, so that the cost of this process is about 1½ time that of the electric method.

Buchner found that sulphide of aluminium, Al_2S_3, is more suitable for the preparation of Al by the electrolytic method than Al_2O_3, but since the formation of Al_2S_3 by heating a mixture of Al_2O_3 and charcoal in sulphur vapour proceeds with difficulty, Gray (1894) proposed to prepare Al_2S_3 by heating a mixture of charcoal, sulphate of aluminium, and sodium fluoride. The resultant molten mixture of NaF and Al_2S_3 gives aluminium directly under the action of an electric current. The production of 1 kilo of aluminium consumes about 30–50 h.p. per hour at the present day. At its present price—three francs per kilo—aluminium can compete with copper in equal volumes.

but also to yield very high temperatures. Thus 'thermite' (Goldsmith) or a mixture of aluminium powder and powdered oxide of iron (see Chap. III., note 42) is used for obtaining high (up to 3000°) temperatures and for welding iron. The reaction proceeds according to the equation: $Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$, and corresponds to the evolution of about 150,000 units of heat per 54 parts of aluminium.[37b] The comparative lightness of aluminium and the great ease with which it takes up oxygen from even the metals of the alkalies are in apparent contradiction to the fact of its being unoxidised by exposure to the air. This is apparently due to a thin, transparent layer of oxide (Ditte) being formed as a coating over the metal, because the metal in the form of powder (the surface is then greater) always contains much oxide. If a solution of corrosive sublimate is poured over metallic aluminium (or even if the metal is simply moistened with the solution) the mercury is reduced and forms an amalgam in which the aluminium becomes oxidised with great ease and decomposes water at the ordinary temperature. This action is probably assisted by the fact that a galvanic couple (mercury-aluminium) is formed, and also by the formation of a renewed bright fresh surface of aluminium (see note 36a). Amalgamated aluminium is prepared (according to Wislicenus, 1895) by pouring a 0·5 per cent. solution of $HgCl_2$ over aluminium powder or shavings previously washed with an alkali, and quickly washing with water, alcohol, ether, and benzene directly hydrogen begins to be given off. The amalgam should be kept under benzene. As it decomposes water with the evolution of hydrogen it may be used as an excellent neutral reducing agent—for instance, for reducing the oxides of nitrogen and nitro-compounds, and also for removing water from alcohol, &c. Dilute sulphuric acid has scarcely any action on Al, but the strong acid dissolves it. Nitric acid also does not dissolve it. On the other hand, hydrochloric acid, caustic potash, and ammonia dissolve aluminium. In the latter cases hydrogen is evolved.[38]

[37b] A mixture of the oxides of Fe, Cr, &c., with aluminium powder may be ignited, according to Goldsmith, by means of special capsules containing a mixture of peroxide of barium and aluminium powder. The capsules burn very violently and rapidly. But 'thermite' may also be ignited directly by means of a magnesium wire set into its midst.

[38] Aluminium, when heated to the high temperature of the electric furnace, dissolves carbon and forms an alloy which, according to Moissan, when rapidly treated with *cold* hydrochloric acid, leaves a compound C_3Al_4 in the form of a yellow crystalline transparent substance of sp. gr. 2·36. This **carbide of aluminium**, C_3Al_4, corresponds to methane, CH_4, for Al replaces H_3 and carbon O_2 or H_4, that is, it is equal to three molecules of CH_4 with the substitution of twelve atoms of H in it by four of Al, or, what is the same thing, it is the duplicated molecule of Al_2O_3 with the substitution of O_6 by C_3. And indeed C_3Al_4 under the action of water forms marsh gas and hydrate of alumina: $C_3Al_4 + 12H_2O = 3CH + 4Al(OH)_3$ This decomposition presents a new aspect of the syn-

Aluminium forms alloys with different metals with great ease. Among them the copper alloy is the only one of practical use. It is called **aluminium bronze.** This alloy is prepared by dissolving 11 per cent. by weight of metallic aluminium in molten copper at a white heat. The formation of the alloy is accompanied by the development of a considerable quantity of heat, so that it glows to a bright white heat. This alloy (Chap. XV., note 19b), which corresponds with the formula $AlCu_3$, presents an exceedingly homogeneous mass, especially if perfectly pure copper is taken. It is distinguished for its capacity to fill up the most minute impressions of the mould into which it may be cast, and by its extraordinary elasticity and toughness, so that objects cast from it may be hammered, drawn, polished, &c. A wire made of this alloy, 1 sq. mm. in section, breaks under a load of 60 kilos (almost the same as for steel and greater than with iron and copper) with an elongation of 24 per cent. Its specific gravity is 7·7. Its surface remains almost unchangeable in the air, and it has a colour and lustre which may be compared to that of gold alloys. Hence aluminium bronze is much used in the arts for making spoons, watches, vessels, forks, knives, and for ornaments, &c. No less important is the fact that the admixture of the one-thousandth part of aluminium with steel renders its castings homogeneous (free from cavities) to an extent that could not be arrived at by other means; nor does the quality of the steel deteriorate in any respect by this admixture, but rather is it improved. In a pure state, aluminium is only employed for such objects as require the hardness of metals with comparative lightness, such as telescopes and various physical apparatus and small articles, &c. Among the alloys of aluminium, **magnalium**, containing from 10 to 25 per cent. of magnesium, deserves to be mentioned, as it is lighter than aluminium, having the sp. gr. about 2·2. It is unchangeable in the air, is easily cast, hard and tough, and takes so fine a polish that it can be used for making mirrors (when it contains about 20 per cent. Mg).

According to the periodic system of the elements, the analogues of magnesium are zinc, cadmium, and mercury in the second group. So also in the third group, to which aluminium belongs, we find its corresponding analogues **gallium, indium,** and **thallium.** They are all three so rarely and sparingly met with in nature that they could only be discovered by means of the spectroscope. This fact shows that they

---

thesis of hydrocarbons, and quite agrees with what should follow from the action of water upon the metallic carbides as applied by me for explaining the origin of naphtha (Chap. VIII., notes 57, 58, and 69). Frank (1894) by heating Al with carbon obtained a similar although not quite pure compound, which (like CaC_2) evolves acetylene with hydrochloric acid, and hence probably has the composition AlC_3.

are partially volatile, as should be the case according to the properties of their nearest neighbours, the very volatile zinc, cadmium, and mercury. As with them, in gallium, indium, and thallium the density of the metal, decomposability of compounds, &c., rise with the atomic weight. But here we find a peculiarity which does not exist in the second group. With magnesium, zinc, cadmium, and mercury, the fusibility increases with the atomic weight; indeed, the heaviest metal—mercury—is a liquid. In the third group it is not so. In order to understand this it is sufficient to turn our attention to the elements of the further groups of the uneven series—for instance, to group V., containing phosphorus, arsenic, and antimony, or to group VI., with sulphur, selenium, and tellurium, and also to group VII., where chlorine, bromine, and iodine are situated. In all these instances the fusibility decreases with a rise of atomic weight; the members of the higher series, the elements of a high atomic weight, fuse with greater difficulty than the lighter elements. The elements of the uneven series of group III., aluminium, gallium, indium, thallium, forming, as they do, a transition, all show an intermediate behaviour. Here the most fusible of all is the medium metal gallium,[38a] which fuses at the heat of the hand; whilst indium, thallium, and aluminium fuse at much higher temperatures.

Zinc (group II.), which has an atomic weight 65, should be followed in group III. by an element with an atomic weight of about 69. It will be in the same group as Al, and should consequently give R_2O_3, RCl_3, $R_2(SO_4)_3$, alums, and similar compounds analogous to those of aluminium. Its oxide should be more easily reducible to metal than alumina, just as zinc oxide is more easily reduced than magnesia. The oxide R_2O_3 should, like alumina, have feeble but clearly expressed basic properties. The metal reduced from its compounds should have a greater atomic volume than zinc, because in the fifth series, proceeding from zinc to bromine, the volume increases. And as the volume of zinc is 9·2, and that of arsenic 18, our metal should have a value near to 12. This is also evident from the fact that the volume of aluminium is 11, and that of indium 14, and our metal is situated in group III., between aluminium and indium. If its volume is 11·5, and its atomic weight about 69, then its density will be nearly 5·9. The fact that zinc is more volatile than magnesium gives reason for thinking that the metal in question will be more volatile than

---

[38a] The same is the case in group IV. of the uneven series, where tin is the most fusible. Thus the temperature of fusion rises on both sides of tin (silicon is very infusible; germanium, 900°; tin, 230°; lead, 326°); as it also does in group III., starting from gallium, for indium fuses at 176°, less easily than gallium but more easily than thallium (294°). Aluminium also fuses with greater difficulty than gallium.

aluminium, and therefore for expecting its discovery by the aid of the spectroscope, &c.

These properties were indicated by me for the analogue of aluminium in 1871, and I named it (see Chap. XV.) **eka-aluminium.** In 1875 Lecoq de Boisbaudran, who had done much work in spectrum analysis, discovered a new metal in a zinc blende from the Pyrenees (Pierrefitte). He recognised its individuality and difference from zinc, cadmium, indium, and the other companions of zinc by means of the spectroscope ; but he only obtained some fractions of a centigram of it in a free state. Consequently only a few of its reactions were determined, as, for instance, that barium carbonate precipitates the new oxide from its salts (alumina, as is known, is also precipitated). Lecoq de Boisbaudran named the newly discovered metal **gallium.** As one would expect the same properties for eka-aluminium as were observed in gallium, I pointed out this fact at the time in the 'Memoirs' of the Paris Academy of Sciences. All the subsequent observations of Lecoq de Boisbaudran confirmed the identity between the properties of gallium and those indicated for eka-aluminium. Immediately after this the ammonium alum of gallium was obtained, but the most convincing proof of all was found in the fact that the density of gallium, although first apparently different (4·7) from that indicated above, afterwards, when the metal was carefully purified from sodium (which was first used as a reducing agent), proved to be just that (5·9) which would have been looked for in the analogue of aluminium; and, what was very important, the equivalent (23·3) and atomic weight (69·8) determined by the specific heat (0·08) were shown by experiment to be such as would be expected. These facts confirmed the universality and applicability of the periodic system of the elements. It must be remarked that previous to it there was no means of foretelling either the properties or even the existence of undiscovered elements.[39]

Much more light has been thrown on the following element of the

---

[39] The spectrum of gallium is characterised by a brilliant violet line of wave-length = 417 millionths of a millimetre. The metal can be separated from the solution, containing a mixture of the many metals occurring in the zinc blende, by making use of the following reactions: it is precipitated by sodium carbonate in the first portions; it gives a sulphate which, on boiling, easily changes into a basic salt, very slightly soluble in water; and it is deposited in a metallic state from its solutions by the action of a galvanic current. It fuses at +30°, and, when once fused, remains liquid for some time. It oxidises with difficulty, evolves hydrogen from hydrochloric acid and from potassium hydroxide, and, like all feeble bases (for instance, alumina and indium oxide), it readily forms basic salts. The hydroxide is soluble in a solution of caustic potash, and slightly so in caustic ammonia. Gallium forms volatile $GaCl_3$ and $GaCl_2$ (Nilson and Pettersson).

aluminium group, **indium**, In, which occurs in small quantities in certain zinc ores. It was discovered (1863) by Reich and Richter (and more fully investigated by Winkler) in the Freiberg zinc ores, and was named indium from the fact that it gives to the flame of a gas-burner a blue coloration, owing to the indigo blue spectral lines proper to it (wave-length 451 millionths of 1 mm.). The equivalent (see Chap. XV., note 15), specific heat, and other properties of the metal confirm the atomic weight In = 114 and the composition of its oxide InO_3.[40]

Inasmuch as we found among the analogues of magnesium in group II. a metal, mercury, heavier and more easily reduced than the rest, and giving two degrees of oxidation, so we should expect to find among the analogues of aluminium in group III. a metal which would be heavy, easily reduced, and give two grades of oxidation, and would have an atomic weight greater than 200. Such is **thallium.** It forms compounds of a lower type, TlX, besides the higher unstable type TlX_3, just as mercury gives HgX_2 and HgX. In the form of thallic oxide, Tl_2O_3, it gives a feebly energetic base, as would be expected by analogy with the oxides Al_2O_3, Ga_2O_3, and In_2O_3, whilst in thallous oxide, Tl_2O, the basic properties are sharply defined, as might be expected according to the properties of the type R_2O (Chap. XV.). **Thallium** was discovered in 1861 by Crookes and by Lamy in certain pyrites. When pyrites are employed in the manufacture of sulphuric acid, they are burned, and give, besides sulphurous anhydride, the vapours of various substances which accompany the sulphur and are volatile. Among these substances arsenic and selenium are found, and, together with them, thallium. These substances accumulate in a more or less considerable quantity in the tubes through which the vapours formed in the combustion of the pyrites have to pass. When the methods of spectrum analysis were discovered (1860), a great number of substances were subjected to

---

[40] The vapour density of indium chloride, $InCl_3$ (note 31), determined by Nilson and Pettersson, confirms this atomic weight. Indium is separated from zinc and cadmium, with which it occurs, by taking advantage of the facts that its hydroxide is insoluble in ammonia, that the solutions of its salts give indium when treated with zinc (hence indium is dissolved after zinc by acids) and that they give a precipitate with hydrogen sulphide even in acid solutions. Metallic indium is grey, has a sp. gr. of 7·42, fuses at 176°, and does not oxidise in the air; when ignited it first gives a black suboxide, In_4O_3, then volatilises and gives a brown oxide, In_2O_3, whose salts, InX_3, are also formed by the direct action of acids on the metal, hydrogen being evolved. Caustic alkalies do not act on indium, from which it is evident that it is less capable of forming alkaline compounds than aluminium is; however, with potassium and sodium hydroxides, solutions of indium salts give a colourless precipitate of the hydroxide, which is soluble in an excess of the alkali, like the hydroxides of aluminium and zinc. Its salts do not crystallise. Nilson and Pettersson (1889), by the action of HCl upon In, obtained volatile, crystalline, $InCl_2$, and by treating this compound with In, InCl also.

spectroscopic research, and it was observed that those sublimations which are obtained in the combustion of certain pyrites contained an element having a very sharply defined and characteristic spectrum—namely, in the green portion of the **spectra** it gave a well-defined **green band** (wave-length 535 millionths millimetre) which did not correspond with any then known element.[41]

Under the action of a galvanic current solutions of thallium salts deposit the metal in the form of a heavy powder. It is of a grey colour like tin, is soft like sodium, and has a metallic lustre. Its specific gravity is 11·8, it melts at 290°, and volatilises at a high temperature. When heated slightly above its melting-point it forms an insoluble (in water) higher oxide, Tl_2O_3, as a dark-coloured powder, generally, however, accompanied by the lower oxide Tl_2O, which is also black, but soluble in water and alcohol. This solution has a distinctly

---

[41] Thallium was afterwards found in certain micas and in the rare mineral crookesite, containing lead, silver, thallium, and selenium. Its isolation depends on the fact that in the presence of acids thallium forms thallous compounds, TlX. Among these compounds the chloride and sulphate are only slightly soluble, and give with hydrogen sulphide a black precipitate of the sulphide, Tl_2S, which is soluble in an excess of acid, but insoluble in ammonium sulphide. The best method of preparing thallous hydroxide, $TlOH$, is by the decomposition of the requisite quantity of baryta by thallous sulphate, which is slightly soluble in water; barium sulphate is then obtained in the precipitate and thallous hydroxide in solution. This solubility of the hydroxide is exceedingly characteristic, and forms one of the most important properties of thallium. These lower (thallous) compounds are of the type TlX, and recall the salts of the alkalies. The salts TlX are colourless, do not give a precipitate with the alkalies or ammonia, but are precipitated by ammonium carbonate, because thallous carbonate, Tl_2CO_3, is sparingly soluble in water. Platinic chloride gives the same kind of precipitate as it does with salts of potassium—that is, thallous platinichloride, $PtTl_2Cl_6$. All these facts, together with the isomorphism of the salts TlX with those of potassium, again point out what an important significance the types of compounds have in the determination of the character of a given series of substances. Although thallium has a greater atomic weight and greater density than potassium, and although it has less atomic volume, nevertheless thallous oxide is analogous to potassium oxide in many respects, for they both give compounds of the same type, RX. We may further remark that thallous fluoride, TlF, is readily soluble in water, as also is thallous silicofluoride, $SiTl_2F_6$, but that thallous cyanide, $TlCN$, is sparingly soluble in water. This, together with the slight solubility of thallous chloride, $TlCl$, and sulphate, Tl_2SO_4, indicates an analogy between TlX and the salts of silver, AgX.

As regards the higher oxide or the **thallic oxide**, Tl_2O_3, the thallium is trivalent in it—that is, it forms compounds of the type TlX_3. The hydroxide, $TlO(OH)$, is formed by the action of hydrogen peroxide on thallous oxide, or by the action of ammonia on a solution of thallic chloride, $TlCl_3$. It is obtained as a brown precipitate, insoluble in water but easily soluble in acids, with which it gives thallic salts, TlX_3. **Thallic chloride**, $TlCl_3$, which is obtained by cautiously heating the metal in a stream of chlorine, forms an easily fusible white mass, which is soluble in water and able to part with two-thirds of its chlorine when heated. An aqueous solution of this salt yields colourless crystals containing one equivalent of water. It is evident from the above that all the thallic salts can be easily reduced to thallous salts by reducing agents such as sulphurous anhydride, zinc, &c. Besides these salts, thallic sulphate, $Tl_2(SO_4)_3,7H_2O$, thallic nitrate, $Tl(NO_3)_3,4H_2O$, &c., are known. These salts are decomposed by water, like the salts of many feebly basic metals—for example, aluminium.

alkaline reaction. This **thallous oxide** melts at 300°, and is easily obtained from the hydroxide, TlHO, by igniting it without access of air (in the presence of air the incandescent thallous oxide passes partly into thallic oxide). **Thallous hydroxide**, TlOH, crystallises with one molecule of H_2O in yellow prisms which are very easily soluble in water. Metallic thallium may be used for its preparation, as the metal in the presence of water attracts oxygen from the air and forms the hydroxide. But metallic thallium does not decompose water, although it gives a hydroxide which is soluble in water. All the other data for the chemical and physical properties of thallium, of its two degrees of oxidation and of their corresponding salts, are expressed by the position occupied by this metal in virtue of its atomic weight Tl = 204, between mercury Hg = 200, and lead Pb = 207.

Gallium, indium, and thallium belong to the uneven series, and there should be elements of the even series in group III. corresponding with calcium, strontium, and barium in group II. These elements should in their oxides, R_2O_3, present basic characters of a more energetic nature than those shown by alumina, just as calcium, strontium, and barium give more energetic bases than magnesium, zinc, and cadmium. Such are **scandium, yttrium**, and **lanthanum**, the atomic weights of which are greater than those of Ca, Sr, and Ba, and which give ordinary oxides of the composition R_2O_3, and are subject to the periodic grouping of the elements in all other respects. However, they are accompanied in nature by a whole series of other elements among which **cerium**, Ce=140, and **thorium**, Th=232, must be referred to group IV., but which all have so many points in common that they have long been classed under a special group of **elements of the rare earths**, so called from the comparative rarity of the minerals from which they are extracted and from the fact that their saline oxides of the composition R_2O_3 and RO_2 are analogous to such earths as CaO and Al_2O_3. The best known, besides the five above-mentioned elements (Sc, Y, La, Ce, and Th) which have their corresponding places in the periodic system, are *ytterbium* Yb=173, which apparently has its proper place in group III. in the 10th series, then praseodymium, Pr=141 and neodymium, Nd=144, one of which apparently belongs to group V. and the 8th series. The other elements of the rare earths are hardly known in a pure form, and if their basic oxides be given the composition R_2O_3 they should belong to group III. It seems to me that new and more complete researches are necessary before any true judgment can be formed about these elements. The great authority on these elements, Professor **B. F. Brauner**, of Prague, has at my request written a special description of them for this book, and I am happy to be able to embellish my work with his concise but detailed account of these metals of the rare earths. The metal cerium is treated with the rest, although, like thorium, it strictly belongs to group IV.

THE ELEMENTS OF THE RARE EARTHS.

PROF. B. BRAUNER.

The discovery of the rare earths.—In 1794 Gadolin discovered a new earth or oxide, which Ekkeber named *yttria*, the mineral now known as Gadolinite occurring at Ytterbi, near Stockholm. In 1803 Berzelius and Gisinger, and at the same time Klaproth, discovered a new oxide, which the Swedish chemist named a 'cerium earth,' in cerite, or the 'heavy stone of Bastenaus.' In 1839 Mozander found that it contained *lanthanum*, and in 1842 he found that this lanthanum, which gives colourless salts, contains an earth forming rose-coloured salts, which was named oxide of didymium. In 1848 Mozander decomposed yttria into three different earths by a method of fractional precipitation with ammonia and acid oxalate of potassium.

The first gives colourless salts and retained the name of yttria; the second gave pink salts and was called the oxide of terbium; and the third, which gave a dark-yellow peroxide and colourless salts, was called erbia. In the beginning of the sixties Berlin, and a little later Bar and Bunsen, found that the acid mixture formerly called yttria contained, besides Mozander's yttria, yet another earth forming pink salts, which they named erbia. And when after this Delafontaine found a third yellow earth in Mozander's earth, it was called terbia.

More recent researches have led to the discovery of a whole series of oxides of new elements in the gadolinite earths. Thus Delafontaine's phillipium (which Roscoe thought a mixture) and decipium (1878) partly correspond with samarium discovered in 1879 by Lecoq de Boisbaudran in the didymium obtained from Samarskite, and Smith's mozandrium with terbium. In 1878 Marignac investigated the oxide of erbium discovered by Bar and Bunsen and separated from it a white earth giving colourless salts and containing an element he named ytterbium. At the same time Soret also discovered a new element in oxide of erbium which he called X. In 1879 Nilson confirmed the existence of the ytterbium discovered by Marignac, and split up the oxide then known as oxide of ytterbium into the true oxide of ytterbium and a new earth whose element he called scandium. In 1879 Clève showed that the oxide, which was then known as oxide of erbium, in reality consists of three earths. One of these contains the element holmium, which resembles Soret's X, another pure erbium, and the third thulium. In 1886 Lecoq de Boisbaudran showed that oxide of holmium also contains oxide of dysprosium.

In 1880 Marignac investigated the earths of samarskite and discovered two new earths in them, the oxides of $Y\alpha$ and $Y\beta$. In 1886 the oxide of $Y\alpha$ was termed 'gadolinia.' The oxides of $Y\beta$ proved to be identical with the samarium of Lecoq. In 1901 Demarçay separated a new oxide from samarium, forming colourless salts whose element he called 'europium.'

The researches of Delafontaine, Clève, and Brauner in the eighties showed that the element then known as didymium consisted of several elements, and that portions of the absorption bands of the former didymium corresponded to each of these elements. At the same time Brauner and Clève separated samarium from the didymium of cerite. In 1882 Brauner also showed that the lanthanum of cerite consists of a mixture of two elements. In 1885, Auër von Welsbach succeeded in ultimately decomposing didymium into praseodymium, giving green salts, and neodymium, giving rose-coloured salts. The most recent researches of Crookes, Krüss, Nilson, Demarçay, and others apparently show that neodymium consists of a mixture of several elements. Furthermore, Krüss and his assistants showed that the oxides of erbium, holmium, and terbium consist of several very similiar earths. An investigation of the spectra of phosphorescence given by several of these rare earths under the action of an electric discharge *in vacuo* (or else by the action of cathodic or dark radiation) led Crookes to the conclusion that the former oxide of yttrium contained several new elements. Lecoq de Boisbaudran (1885) is not of this opinion, and thinks that holmium, terbium, and samarium contain yet other new elements. One of these is europium, discovered by Demarçay.

The occurrence of the rare earths in nature.—They are only found in compounds forming rather rare minerals. In some of these minerals the cerite earths (see later), designated by [Ce] in the context, predominate, while in others the yttrium earths subsequently designated by [Y] predominate, but frequently both these earths occur simultaneously. Over fifty minerals containing the rare elements are known. We shall only enumerate the chief of these. *Silicates*, [Ce], cerite, orthite, allanite ; [Y], gadolinite, yttrialite ; [Ce, Y], tritolite. *Carbonates* : [Ce], lanthanite ; and containing fluorine, parasite, hamartite. *Phosphates* : [Ce], monazite (containing Th), rabdophane [Y], xenotime. *Fluorides* : [Ce], fluocerite ; [Y], yttrocerite. *Silico-titanites* : [Ce], cheokinite, mosandrite ; [Y], keilhauite. *Titano-niobium compounds* : [Ce], æschynite, pyrochlore. *Tantalo-niodium compounds* : [Y], siphilite, tyrite, yttro-tantalite, samarskite, euxenite ; [Y, Ce], fergusonite (contains He), cleveite, bröggerite, and nivenite, besides the rare earths, contain uranium, thorium, lead, and also, like some of the above minerals, helium. Besides these, the rare earths occur in small quantities in many minerals, such as apatite, strontianite, and serpentine ; in coprolites, in the ash of tobacco and bones, and in urine (Cossa). When Auër showed that a mixture of the oxides of thorium and cerium may be employed in incandescent lamps for lighting purposes, the rare earths were sought for in different localities, and a source for their exploitation was found in the comparatively larger deposits of monazite occurring in Brazil and North Carolina, and this has given the possibility of extending our knowledge of the rare earths in recent years. The lines of Y, Er, and La, and perhaps Ce, have been detected in the solar spectrum.

The atomic composition of the rare earths.—Prior to the close of the sixties it was held that the rare earths which exhibit clearly basic properties (this chiefly refers to the oxide of lanthanum, the hydrate of the suboxide of cerium, and the oxides of yttrium, erbium, and didymium then known) form compounds of the type RO like the oxides of the metals of the alkaline earths. The higher oxide of cerium was then given the formula Ce_3O_4, like the compounds Mn_3O_4 and Fe_3O_4. According to their analogies and types RO, the following atomic weights were ascribed to the metals of the rare earths : $Y = 61·7$, $Ce = 92$, $La = 90–94$ $Di = 95$, $Er = 112·7$—that is, they were considered to be divalent with respect to hydrogen. After having established his periodic system, Mendeléeff (1870) observed that the elements of the rare earths do not fit into the general order of the elements if the above atomic weights are adopted, and that if the higher oxide of cerium be regarded as a compound of two oxides, CeO, Ce_2O_3, account must be rendered of the fact that one of these oxides, namely, Ce_2O_3, and its corresponding salts are not obtainable. As the amounts of oxygen in the two known oxides of cerium (CeO and Ce_3O_4, if $Ce = 92$) are in the ratio 3 : 4, Mendeléeff proposed the formulæ Ce_2O_3 and Ce_2O_4 or CeO_2 for the two oxides. In this case the true atomic weight of cerium would be three times the hydrogen equivalent, $46 \times 3 = 138$, and then this element would find a place in group IV., in the 8th series; the properties of cerium and its compounds were found to correspond with such a position among the other elements.

Mendeléeff even foresaw a higher atomic weight, about 140, for pure cerium, and also the possibility of the existence of CeF_4; and Brauner's subsequent researches entirely confirm his prediction. Moreover, Mendeléeff determined the specific heat of metallic cerium, and found it to be equal to 0·05, which, multiplied by the new atomic weight, is equal to 6·9, or very nearly the normal atomic specific heat. Hillebrand (1876) made fresh determinations, and obtained a value 0·0448, which gives the atomic specific heat 6·3. With respect to didymium and lanthanum, Mendeléeff could not arrive at a decisive conclusion, as only *one* element with an atomic weight of about 140 could be conveniently placed in group III. (oxide of type R_2O_3). He therefore considered it possible to accept the formulæ of the oxides as R_2O_3 for one, and RO_2 for the other of these elements. Subsequently Mendeléeff adopted the type R_2O_3 for the oxides of both metals, and only placed lanthanum in his system by the side of Ce. For the little investigated elements Y and Er, Mendeléeff (1870) adopted the atomic weights : $Y = 88$ and Er = about 178, and gave them the positions III., 6 and III., 10 in his periodic system. The researches of Clève and Höglund (1873) on yttrium and erbium, of Clève (1874) on yttrium, erbium, didymium, and lanthanum, of Tolin (1875) on cerium, and Hillebrand (1876) on the specific heats of Ce, La, and Di, showed the atomic weight of La to be 138 − 139, and that of Di 144, the formulæ of the oxides being La_2O_3 and Di_2O_3.

Subsequently, Marignac, Clève, Nilson, Krüss, Brauner, and their assistants, Jones, von Scheele, Benedix, Muthmann and his assistants, Coppel, and others, investigated the elements of the rare earths, and their researches still further confirmed Mendeléeff's views, so that the composition of the chief basic oxides or earths is now expressed by the formula R_2O_3. Thus one chief common type RX_3 is accepted for the elements of the rare earths. The higher existing oxides of Ce, Pr, and Nd are given the formula R_2O_4, that is, they are looked upon as compounds of the type RX_4. Although the vapour density of none of the compounds of the metals of the rare earths is known (owing to their not being volatile), still other physical data have been obtained, besides the specific heats of Ce, La, and Di (or, more strictly speaking, of the mixture of Pr and Nd) and give the requisite means for determining the atomic composition of the compounds of these elements.

The boiling-points of their solutions (Chap. VII., laws of Raoult and van't Hoff) confirm the molecular compositions $CeCl_3$ (Muthmann), $PrCl_3$ (Brauner), and $NdCl_3$ (Matignon). But the atomic weights of the remaining elements of the rare earths can as yet only be judged by analogy by studying the composition of corresponding salts, such as the chlorides, sulphates, and nitrates, &c., according to the researches of Clève, of the double platinum salts according to Nilson, of the double sulphates of cerium according to Brauner, and of the acid sulphates also according to Brauner.[1]

Another important reason for taking the composition of the oxides as R_2O_3 is the isomorphism of the monoclinic sulphates of yttrium, praseodymium, neodymium, samarium, terbium, erbium, and ytterbium, of the composition $R_2(SO_4)_3,8H_2O$. Moreover, the corresponding sulphate of cerium crystallises in the rhombic system, and is not isomorphous with the preceding salts, and the sulphates of scandium and lanthanum do not give hydrates with $8H_2O$, but with $6H_2O$ and $9H_2O$ respectively. Further, the values expressing the solubilities of the oxalates in a normal solution of sulphuric acid (i.e., one containing 49 grms. of H_2SO_4 per litre of water), and in a solution of ammonium oxalate are of the same order for those of the above elements which give R_2O_3 and for other compounds known to belong to the type RX_3, whilst the corresponding solubility for thorium compounds of the type RX_4 is of quite another order.

The position occupied by these elements in the periodic system gives a means for testing the truth of the atomic weights of scandium and yttrium (besides those of lanthanum and cerium, which have been firmly established on the basis of physico-chemical data; but for the remaining elements there are no physico-chemical data for forming any conclusion in this respect, as mentioned at the end of this chapter).

Characteristic properties and reactions.—The elements of the rare earths not only occur together in nature, but they also closely resemble each other in their chemical relations. The only ones which have been obtained in a free metallic state are Ce, La, Nd, and Y, prepared by the electrolysis of their chlorides, or in a less pure form by the action of Na on their chlorides or of Mg on their oxides. If they are reduced from their oxides in a stream of hydrogen they form hydrides in the form of a black powder. The metals remain unaltered in dry air, but easily become oxidised in damp air, especially if the temperature be raised. In the form of powder they burn with a brilliant light. The oxides of the form R_2O_3 are mostly somewhat powerful bases, but the basic properties of La_2O_3 and Y_2O_3 (they combine directly with water and readily absorb CO_2 from the air)

---

[1] Great caution is required in drawing such conclusions 'by analogy,' as it is easy to fall into error. For instance, while the atomic weight of beryllium *appeared* yet doubtful, Nilson and Pettersen cited the analogy of many of the salts of oxide of beryllium and of alumina as a proof that Be = 13·6, and that its oxide was Be_2O_3. Now it is known that this *apparent* analogy proceeds from the fact that beryllium forms a link between groups II. and III.

are much more energetic than those of Yb_2O_3 and Sc_2O_3. With the exception of CeO_2, Yb_2O_3, and Sc_2O_3, they all dissolve easily in cold acids and evolve much heat in so doing. The anhydrous sulphates, $R_2(SO_4)_3$, are readily soluble in ice-cold water and easily give supersaturated solutions. At a somewhat higher temperature these solutions deposit hydrated sulphates which dissolve with difficulty in cold water, and are still less soluble in hot water. The chlorides, RCl_3, bromides, RBr_3, and iodides, RI_3, are very hygroscopic and readily soluble in water. The same may be said of the nitrates, $R(NO_3)_3$. The fluorides, RF_3, are insoluble in water, as also are the carbonates and phosphates. The sulphides, R_2S_3, decompose in dissolving in water, and form a hydroxide, $R(OH)_3$, and H_2S. Carbides are formed when the oxides are heated with carbon in the electric furnace. The carbides, when treated with water, give a mixture of acetylene, ethylene, methane, and other gaseous, liquid, and solid hydrocarbons (Moissan and others).

Aqueous solutions of the salts of the rare earths are not precipitated by H_2S. With ammonia they give amorphous precipitates of basic salts. Caustic soda precipitates the hydroxides, which readily absorb CO_2 from the air and are insoluble in an excess of alkali. Sulphide of ammonia acts like free ammonia. The carbonates of the alkali metals precipitate amorphous carbonates. Powerful bases (like La_2O_3) are insoluble in an excess of the reagent; but the less energetic the basic properties, the greater is the facility with which they are dissolved by an excess of the carbonate of the alkali metal. Carbonate of ammonium is a better solvent than carbonate of potassium. Oxalic acid and the oxalates give voluminous precipitates having the composition $R_2(C_2O_4)_3,xH_2O$, which after a time become crystalline. These precipitates are but slightly soluble in the mineral acids, but as a rule, the more soluble they are the greater is the energy of the base. They dissolve feebly in an excess of oxalate of ammonium, but generally speaking the solubility increases as the base becomes weaker. With peroxide of hydrogen in the presence of alkalies, they give precipitates of hydrated peroxides, R_2O_5,xH_2O, which as a rule are of the same colour as the hydroxides. Only the salts of cerium give a hydrated peroxide CeO_3XH_2O of the same colour as hydrated oxide of iron. All the sulphates of this group form, with sulphate of potassium, double salts, having mostly the composition $3K_2SO_4,R_2(SO_4)_3$. *These elements are divided into two groups* according to the solubility or insolubility in a solution of sulphate of potassium. The double sulphates of the *cerite metals* are quite insoluble or dissolve with difficulty in a saturated solution of K_2SO_4. These include La, Ce, Pr, Nd, Sm, Eu, and Sc. The double sulphates of *potassium and the gadolinite metals* are more easily, or even very, soluble in a saturated solution of K_2SO_4. These include Y, Gd, Tb, and Yb, and the mixtures known as holmium, erbium, and thulium. The formates of the cerite metals also dissolve with difficulty in water; while the same salts of the gadolinite elements, i.e., the anologues of yttrium, are easily soluble. Benedix showed that the platino-cyanides of the cerite metals crystallise in yellow crystals with a blue metallic lustre. The platinocyanides of the yttrium metals are cherry-coloured, with a green metallic lustre. In the colour and form of its platino-cyanides, gadolinium belongs to the yttrium elements.

Cerium and praseodymium form two kinds of oxides. The lower corresponds to the other rare earths in its form, R_2O_3. The higher oxides of cerium and praseodymium are formed after the type R_2O_4. They form salts of the type RX_4, but those of praseodymium are very unstable. The oxides, R_2O_4, of cerium and praseodymium are obtained by fusing their nitrates with nitre, and the oxide C_2O_4 is also obtained by calcining the oxalates and sulphates of the lower form CeX_3. The hydroxide of the higher oxide of cerium, $Ce(OH)_4$, is a much weaker base than $Ce(OH)_3$. The former is obtained by the action of chlorine on $Ce(OH)_3$ in the presence of caustic potash. The salts of the higher form, CeX_4, are yellow, orange-yellow, and brownish-yellow in colour and form yellow solutions with a small amount of water, but hydrolytic decomposition takes place in the presence of a larger amount of water and basic salts are precipitated. Alkalies precipitate the hydroxides or basic salts from these solutions. Carbonate of ammonium gives a yellow precipitate soluble in an excess of the reagent. The addition of peroxide of hydrogen causes the solution to become red, and a corresponding double salt of potassium and peroxide of cerium is formed. Atmospheric oxygen acts like H_2O_2, only more slowly. In acid solutions, reducing agents, such as sulphurous acid, oxalic acid, ferrous salts, H_2O_2, &c., convert the yellow salts of the higher oxide of cerium, CeX_4, into colourless salts of the lower form, CeX_3, and potassium permanganate or persulphate converts CeX_3 into CeX_4.[2]

It follows, therefore, that, in distinction from all the other metals of the rare earths (excepting thorium) forming oxides R_2O_3 and salts RX_3, only cerium gives a still higher oxide, CeO_2, and corresponding salts, CeX_4. In this respect the as yet little known praseodymium approaches cerium (Brauner).

Owing to the great similarity in their properties and reactions, the separation and distinction of the rare earths from each other have many peculiarities. The following methods are employed for distinguishing them from each other.[43] **The method of determining their atomic weights.** The oxides of the type R_2O_3, obtained by igniting the oxalates, are weighed, dissolved in nitric acid, and mixed with a small excess of sulphuric acid, evaporated, and heated to 600° to drive off the excess of acid. The sulphates of such powerful bases as La_2O_3 are able to withstand this high temperature, whilst those of the weaker bases are decomposed at a temperature of 440° with the partial formation of basic salts. This method of determining the atomic weights (strictly speaking equivalents) was repeatedly used and was the source of those errors which were discovered by Brauner and Pavlichek, and which proceed from the possibility of the formation, under these conditions, not only of the neutral salt, $R_2(SO_4)_3$, but also of the acid salt, $R_2(SO_4)_3,3H_2SO_4$, which lowers the atomic weight. But the true atomic weight may be calculated (Brauner and Pavlichek) from that given by this method, either by determining the amount of sulphuric acid (by titration), or by calcining until the basic salt begins to be formed and then determining the weight of SO_3 wanting. If the basic properties of the R_2O_3 under investigation be weaker, the anhydrous sulphate may be first obtained by heating to 440°,

---

[2] The hydrate of cerium peroxide, CeO_3, is formed not only by H_2O_2 in the presence of alkalies, but also in the presence of the acetates of the alkali metals.

and thus converted into the oxide R_2O_3 by strongly igniting it. In the case of cerium (and also thorium), the oxide R_2O_4 is obtained in this manner (Brauner, Nilson, Krüss). The determination of the atomic weight not only forms an important distinguishing feature for each separate element, but also gives, from the variation of the values obtained at different stages of the separation, a means for following the course of separation and purification in the fractional treatment of a mixture of two or more mixed oxides.

2. **The luminous spectra of electric sparks.**—If the sparks from a large induction coil connected with Leyden jars be caused to pass between carbon or platinum electrodes moistened with a solution of one of the chlorides of this group, and be examined through the spectroscope, it will be found that each element gives its characteristic spectrum with a large number of lines, which render it possible, not only to determine the element, but also to indicate its degree of separation and purity. The spectra of the metals of the rare earths have been tabulated by Thalén, Bunsen, Lecoq de Boisbaudran, Brauner, Auër, Hartley, Demarçay, and Crookes.

3. **Absorption spectra.**—In 1858 Gladstone discovered that when white light is passed through a solution of didymium salt into the spectroscope it gives an absorption spectrum with many dark bands. Later, Delafontaine, Bar and Bunsen, Thalén, Lecoq de Boisbaudran, Brauner, Krüss and Nilson, Crookes, Demarçay, Auër von Welsbach, Becquerel, Urbain, Muthmann, Forsling, and others investigated the absorption spectra of solutions of all the rare earths. It has already been mentioned that the composite compositions of the former didymium and erbium, and the elements praseodymium, neodymium, samarium, &c., were discovered by this means. Soret finds that some colourless salts which do not yield simple absorption spectra exhibit characteristic absorption lines in the ultra-violet portions of their spectra. The investigation of absorption spectra is particularly important and useful in separating and purifying the earths, but it must be borne in mind that the position and intensity of the bands vary with solutions of *one and the same earth* according to the concentration of the solution, the nature of the acid radicle, and the amount of free acid.

4. Special luminous linear spectra which sometimes differ from the ordinary spark spectra are obtained, according to Lecoq de Boisbaudran, if the positive pole of the Ruhmkorff coil be immersed in the solution of a chloride, and the negative pole be fixed directly over the surface of the liquid. The spectra obtained in this manner resemble Crookes's spectra of phosphorescence. The existence of the new elements, holmium, terbium, and samarium, was indicated by this method.

5. **Spectra of phosphorescence and cathodic radiation.**—In 1883 Crookes observed that the basic sulphates of certain rare earths, or even the earths themselves, become phosphorescent when they are subjected to the actions of an electric discharge in an almost perfect vacuum, and that the light so obtained gives spectra with characteristic bands. Crookes thought that he had obtained several elements by fractional decomposition from the old yttrium, and that he had thus discovered the existence of several elements which were apparently analogous to those found by Lecoq de Boisbaudran by the above method. It was afterwards seen that these spectra are extremely

sensitive; that the smallest traces of a foreign substance act on them, so that the conclusions drawn from them by Crookes, Lecoq de Boisbaudran, and others were not generally accepted; for instance, Lecoq says that pure yttrium does not give spectra of phosphorescence. Bettendorf and also Muthmann and Baur subsequently occupied themselves with this subject. The results of their researches in general confirm those obtained by Crookes, but differ from them in details. This method also proved most important for testing the gradual separation of the rare earths from each other. More recently (1901), Baur and Marc found that the oxides or salts of yttrium, gadolinium, and lanthanum do not give broken spectra *when pure.* The spectra previously observed for these elements were due to the presence of small amounts of erbium, neodymium, and praseodymium. This shows that the conclusions drawn from this class of data are still subject to some doubt.

6. **Spectra of radiation from the incandescent earths.**—Bar and Bunsen found that when the earth of erbium is heated to incandescence it emits an intense light, the spectrum of which exhibits light bands corresponding in position with the dark absorption bands. The intensity of the light is increased by the addition of phosphoric acid, but the position of the bands remains unchanged. Oxide of didymium exhibits the same phenomenon, but only with respect to its neodymium constituent. The addition of oxide of erbium and other oxides entirely changes the spectrum. The oxides of samarium and holmium also emit a discontinuous light when heated to incandescence.

Treatment of the minerals for the extraction of the rare earths.—Formerly the cerite earths were almost exclusively extracted from cerite from Bastenaus. This is finely powdered and mixed with strong sulphuric acid. The mixture becomes heated and forms a friable grey powder, which is heated to drive off the excess of sulphuric acid and to decompose the sulphate of iron. The residue is dissolved in chlorine water, and the heavy metals precipitated by hydrogen sulphide, any iron remaining being oxidised with chlorine and hydrochloric acid then added. The solution is then heated and the rare earths are precipitated in the form of oxalates by means of oxalic acid. Auër von Welsbach reduces cerite to a coarse powder, calcines it, treats it with strong hydrochloric acid over a hot water-bath, and evaporates to dryness. The oxalates are precipitated at 50°, well washed, and converted into oxides by igniting in an iron dish.

At the present time about 50–60 per cent. of the cerite oxides and 1–5 per cent. of the yttrium oxides are obtained in the extraction of oxides of thorium from American monazite, which contains about 1–8 per cent. of the thorium earth (ThO_2). The rare earths are here obtained as a by-product or residue, so that impure cerite oxides can now be procured for research in any quantity at a low price.

Gadolinite is the chief source of the gadolinite or yttrium earths. The finely ground mineral is treated with hydrochloric acid, heated, and evaporated. The residue is treated with water and precipitated with oxalic acid. The precipitated salts are washed and ignited with access of air. Euxenite and fergusonite are decomposed by fusing with $KHSO_4$, and the solution poured off from the precipitate of tantalic and niobic acids. Oxalic acid is added to the solution. Samarskite is decomposed with hydrofluoric acid, evaporated, and the residue treated with sulphuric acid, and the aqueous solution precipitated with oxalic acid.

THE SEPARATION OF THE RARE EARTHS.

A. *Separation of cerium.*—Cerium is separated first, in treating a mixture of the rare earths, owing to the ease with which the compounds CeX_3 pass into CeX_4. (1) In the treatment of the *crude yttrium earths* they are dissolved in nitric acid, evaporated, and the nitrates then fused to incipient decomposition. This is done because $Ce(NO_3)_2$ decomposes with the formation of insoluble CeO_2 at temperatures at which the nitrates of the other rare earths remain unchanged, so that they can be extracted by water. (2) In the case of the crude *cerite earths* their oxalates are calcined. A dark reddish-brown powder is obtained, consisting of CeO_2, La_2O_3, the higher oxides of praseodymium and neodymium, together with a small amount of other oxides, and this is dissolved in nitric acid. The separation of the cerium is based upon the fact that water decomposes the salts of the form RX_4, with the formation of insoluble basic salts. The excess of nitric acid is driven off by evaporation from the nitrates, which are then dissolved in a small quantity of cold water. The solution is decanted into a larger quantity of boiling water.[3] The basic salt of the higher oxide of cerium then separates out; it still retains the constituents of didymium, as the latter are also partly converted into salts of the form RX_4. To obtain pure cerium salts, this basic sulphate must be dissolved in sulphuric (Bunsen) or nitric (Brauner) acid and the precipitation with hot water repeated several times. The filtrates from the precipitates of cerium contain some reduced CeX_3, besides other earths of the form RX_3. The CeX_3 is removed by precipitation in the form of oxalate, or by igniting the oxides, dissolving in nitric acid and precipitating CeX_4 by boiling with magnesite (Bunsen), or by Debray's process, which is described later. (3) Cerium may be separated from the other earths by obtaining the oxide CeO_2 from the oxalate in that portion of the solution which contains CeX_4 and boiling it with the remaining solution. The basic salt $CeO_2(CeX_4)_4$ is precipitated (Auër von Welsbach). (4) Cerium salts of the type CeX_4 when mixed with nitrate of ammonium and nitric acid first crystallise out in the form of a double salt $Ce(NO_3)_4,2NH_4NO_3$. The pure cerium salt is obtained by repeating the process (Auër von Welsbach). (5) Debray fuses the impure nitrate of cerium with eight parts of nitrate of potassium at 300-350°, when only nitrate of cerium is decomposed with the formation of CeO_2. The cerium may be further purified by repeating the process. (6) Mozander precipitates a mixed solution of RCl_3 with an excess of caustic potash and passes chlorine through the solution; CeO_2 is precipitated in the form of hydroxide, but it still retains some praseodymium. A pure salt of Ce is obtained by repeating

---

[3] According to Bunsen this water is slightly acidulated with sulphuric acid. Brauner does not add any sulphuric acid. Wyrouboff and Verneuil add ammonium nitrate to the solution.

the process about six times. (7) Poppe adds sodium acetate to a neutral solution of RCl_3 and precipitates the Ce as $Ce(OH)_4$ with chlorine or KOCl. (8) Stolba treats a solution of the impure cerite oxides with $KMnO_4$ in the presence of $Zn(OH)_2$, which gives a precipitate of impure oxide of cerium. If the RCl_3 and $KMnO_4$ be taken with oxide of mercury, then praseodymium and neodymium are also precipitated with the cerium, while lanthanum remains in solution (Winkler). (9) According to Gibbs, the cerium in a mixture of nitrates is first oxidised by boiling with PbO_2 and nitric acid, after which the solution is decomposed with water and the cerium precipitated. (10) The chromates of the rare metals are heated to 110°, only the cerium salt being decomposed at this temperature (Pattinson and Clark). (11) Wyrouboff precipitates the cerium salt in the presence of nitrate or sulphate of ammonium and the cerium remaining in the filtrate with persulphate of ammonium and acetate of sodium. (12) Meyer and Koss separate the cerium, fused with magnesium acetate, by means of peroxide of hydrogen. The hydrate of peroxide of cerium, CeO_2, is then transformed into $Ce(OH)_4$ by boiling.

In all the preceding methods the separation is based upon qualitative differences between the salts CeX_4 and those of the other earths, RX_3. The same principle may be applied to praseodymium. To separate praseodymium from lanthanum, their nitrates are fused with nitre at 400–430°. Only the nitrate of praseodymium is decomposed and separated as Pr_2O_4 (Brauner).

B. *Separation of the remaining rare earths of the type RX_3 from each other.*—This is done in several ways. (1) By means of K_2SO_4. *The cerite earths* form with K_2SO_4 double salts which are insoluble in a saturated solution of the sulphate, whilst the double sulphates of the yttrium earths are soluble. This classical method does not, however, admit of the perfect separation of the two groups, because the solubility is a purely relative factor, which in the case of yttrium attains a maximum of 4·9 grms. Y_2O_3 per 100 vols. of saturated solution of K_2SO_4. Thus, in a mixture of the earths of the two groups, the cerite earths are partially dissolved, while a portion of the yttrium earths remains undissolved. Supersaturated solutions are also easily obtained. Marignac dissolved the double sulphates by a fractional method in a solution of K_2SO_4, and by repeating the process separated the elements $Y\alpha$ (gadolinium) and $Y\beta$ (samarium). Lecoq carried on a fractional separation by precipitating solutions of the sulphates of the earths with K_2SO_4 and alcohol, and succeeded in separating the elements Tb, Dy, Ho, and Er in this way. (2) The *formates* of the cerite earths dissolve with difficulty in water, while those of the gadolinite (yttrium) earths are more easily or even very easily soluble. This method has the inconvenience of easily forming supersaturated solutions. Crystallisation of the acetates sometimes gives the same results (Brauner). (3) Urbain took advantage of the unequal solubility of the aceto-acetic salts and ethyl-sulphonic compounds for separating the rare earths from each other. (4) The *double ammonium nitrates* were first employed by Mendeléeff (1873) for separating lanthanum from didymium. The salt of didymium is the first to crystallise out from a mixture containing both earths. Auër von Welsbach took a similar solution and decomposed the didymium into praseodymium, the double salt of which crystallises out with the double salt of lanthanum, and neodymium, the double salt which remains in the mother liquor. The process of crystallisation must be repeated several times. The neodymium is ultimately recrystallised in the form of a less soluble double salt of sodium, or of sodium and ammonium. As a rule the weaker the basic properties of the earth, the greater the facility with which its double salts dissolve. Demarçay employed the double nitrates of magnesium for separating europium, and also recrystallised the nitrates from strong nitric acid. (5) Mozander took advantage of the difference in solubility in water of the hydrated sulphates for separating lanthanum from didymium. A solution of the anhydrous salts in six parts of ice-cold water deposits chiefly the salt $La_2(SO_4)_3,9H_2O$, when heated to 35°. This process must be frequently repeated, but it is not so good as the Mendeléeff-Auër method. (6) When the oxides (hydroxides) of the earths are heated in a solution of NH_4NO_3 the most powerful base passes into solution to the greatest extent (Marignac, Brauner). (7) The hydroxides are treated by heating in ammonium carbonate solution and the solution then precipitated fractionally with acetic acid. (8) The difference in solubility of the chromates in K_2CrO_4 solution is taken advantage of for separating the earths from each other. (9) *Crystallisation* of a solution of the oxalates in potassium oxalate, the salts of the weakest bases being the most soluble. (10) Decomposition of the nitrates by ignition (Marignac, Berlin, Bar and Bunsen). The nitrates of the weakest bases are more easily decomposed than those of the more energetic bases. But the difference is purely a relative one and the process must be repeated many hundreds of times. Bar and Bunsen separated yttrium and erbium, and Marignac terbium and ytterbium, while Nilson separated scandium from ytterbium, and Clève further decomposed erbium in this manner. In order to separate the cerite earths from each other, Schutzenberger fused their nitrates with nitre, as did Debray (see A, 5). (11) *Fractional precipitation* : (a) by *ammonia* with a mixed solution of the earths. Ammonia first gives a precipitate in which the more feeble bases predominate, while the more energetic bases remain in solution. Several of the earths were obtained pure or were further split up by this method. (b) Caustic potash, magnesia, or an alcoholic solution of aniline may be used instead of ammonia, or even a mixture of the earths themselves may be partly employed as a precipitant after being precipitated with oxalic acid and ignited. (c) *Oxalic acid.* As a rule the earths having the weakest basic properties are concentrated in the first precipitates. Treatment of the oxalates with mineral acids forms a modification of this method. The process of fractional precipitation must be repeated very many times. (12) The application of fractional electrolysis to the separation of the rare earths presents some interest.

As regards the *classification of the elements* of the rare earths and their places in the periodic system, it can now be confidently affirmed that scandium, yttrium, and lanthanum belong to the even series of the third group, as they should do, according to their atomic weights and the volumes of their oxides.

Position	III., 4	III., 6	III., 8
Element	Sc	Y	La
Atomic weight	44	89	139
Volume of R_2O_3	35	45	50

The other elements of the rare earths probably form an inter-periodic group or node in the system, in which they follow each other according to the value of their atomic weights.

Scandium, Sc = 44·1 (Nilson).—The discovery of this element in 1879 by Nilson is of particular interest, because its existence and even its properties were predicted by Mendeléeff in 1871 for ekaboron, which was wanting in the periodic system. This prediction was confirmed in a most brilliant manner, for the atomic weight, 44, was found as predicted; further, the specific gravity of the oxide (predicted 3·5, actual 3·8) and the composition and feeble basic character of its oxide, $Eb_2O_3 = Sc_2O_3$, the difference in the structure of its double salts with sulphate of potassium from that of the alums, and a whole series of other properties and reactions belonging to it as a lower atomic analogue of yttrium, all proved to be identical with those predicted by Mendeléeff. The oxide, Sc_2O_3, is a white powder, dissolving slowly in acids. Its salts are colourless and do not give an absorption spectrum. Alkalies precipitate an amorphous hydrate, $Sc(OH)_3$, from their solutions. Anhydrous $ScCl_3$ is unknown. The sulphate, $Sc_2(SO_4)_3$, crystallises from its solutions with $6H_2O$. Its double salt, $3K_2SO_4,Sc(SO_4)_3$, is insoluble in a solution of K_2SO_4. Oxalic acid precipitates the oxalate, $Sc_2(C_2O_4)_3,6H_2O$, from solutions as a white finely crystalline precipitate. The spark spectrum of the chloride gives over a hundred lines, some of which are very bright. Pure preparations of scandium are exceedingly rare, as 3–4 kilos of gadolinite or yttro-titanite only yield 1 gram of oxide of scandium (Clève).

Yttrium, Y = 89·0 (Jones).—The element has been obtained as a grey powder having the sp. gr. 3·8 (vol. 23·6) by the action of sodium on YCl_3 and also by electrolysis. It is obtained in an impure form from Y_2O_3 by the action of Mg; but if the mixture is heated in a stream of hydrogen it forms a hydride, Y_2H_3. The oxide Y_2O_3 is obtained by calcining the sulphate, nitrate, oxalate, &c. It is a white powder, of sp. gr. 5·046 (vol. 45) which easily dissolves in acids. The salts are colourless and do not give any absorption spectra. Alkalies precipitate the *hydroxide*, $Y(OH)_3$, from solutions of its salts. Peroxide of hydrogen and ammonia give the hydroxide of the higher oxide Y_4O_9 (more likely Y_2O_5). Chloride of yttrium, YCl_3, may be obtained, like all the anhydrous chlorides of the elements of this group, either by evaporating a solution of the oxide in hydrochloric acid with chloride of ammonium and igniting the residue, or by the action of chlorine on a mixture of the oxide and carbon at a red heat. It crystallises from solutions as $YCl_3,6H_2O$. Fluoride of yttrium, YF_3, is amorphous and insoluble in water. Y_2S_3 is a yellowish-grey powder, obtained by heating the oxide in the vapour of carbon bisulphide. The anhydrous sulphate, $Y_2(SO_4)_3$, dissolves readily in water (ice-cold) and crystallises out from solutions as a hydrate, $Y_2(SO_4)_3,8H_2O$, in monoclinic crystals, which are isomorphous with those of the corresponding salts of Pr, Nd, Sm, Tb, Er, Yb. An *acid* salt, $Y_2(SO_4)_3,3H_2SO_4$, is formed by heating the sulphate with sulphuric acid (Brauner and Picek). The double salts with K_2SO_4 are soluble in a saturated solution of K_2SO_4. The nitrate, $Y(NO_3)_3,6H_2O$, forms beautiful crystals which readily deliquesce. The salts: $YPO_4,2H_2O$, $Y_2(CO_3)_3,3H_2O$ and the *double platino-cyanide* $Y_2[Pt(CN)_4]_3,21H_2O$, have also been studied. A *carbide*, YC_2, is obtained, when the oxide is heated with carbon in the electric furnace, as a friable partly crystalline mass which yields a large amount of C_2H_2 and some CH_4, C_2H_4, and H_2 under the action of water. The *spectrum* of the sparks of the chloride is very bright and particularly characteristic in giving two groups containing numerous lines in the red and orange portions of the spectrum.

Lanthanum, La = 139·04 (Brauner).—The purest preparations of lanthanum have been obtained by the combined methods of Mendeléeff, Auër, Debray, Schutzenberger, and by fractional precipitation with caustic potash (Brauner and Pavlichek). It has been obtained in a free state as a grey powder by Mozander by heating $LaCl_3$ with potassium. Hillebrand and Norton obtained it, by the electrolysis of $LaCl_3$, as a dense mass, sp. gr. 6·163, of an iron-grey colour. It easily reacts with dilute halogen acids, and is slowly decomposed by cold, and violently by hot water. A hydride La_2H_3 (?) is formed by heating the oxide with magnesium in a stream of hydrogen. The oxide La_2O_3 is obtained by calcining the oxalate and other salts. It is a white powder which easily dissolves in acids. Its sp. gr is 6·48. It may be slaked with water like lime, forming $La(OH)_3$, which is also precipitated from solutions of the salts by alkalies. It absorbs CO_2 from the air with avidity. With H_2O_2 in the presence of alkalies the salts of lanthanum give a hydrate of the peroxide La_2O_5. The salts of lanthanum are colourless and give no absorption spectra. They are sweet and astringent to the taste.

Chloride of lanthanum, $LaCl_3$, is obtained by heating its double salts with sal-ammoniac, by heating the oxalate with sal-ammoniac or in a stream of hydrochloric acid gas and by heating the sulphides in a stream of hydrochloric acid gas. The hydrate, $2LaCl_3,15H_2O(LaCl_3,7H_2O\ ?)$, crystallises out from a hydrochloric acid solution. The oxychloride, $LaOCl$, is formed by heating the oxide in a stream of chlorine. LaF_3,H_2O is obtained as a gelatinous precipitate. La_2S_3 is obtained by heating the oxide in the vapour of CS_2, or the sulphate in a stream of hydrogen sulphide, and is a yellow powder easily decomposed by water. The anhydrous sulphate, $La_2(SO_4)_3$, is readily soluble in ice-cold water. At ordinary temperatures, $La_2(SO_4)_3,9H_2O$ crystallises out from solutions in acute hexagonal prisms, which are isomorphous with the nonahydrated salt of cerium; at 0° the hydrate $La_2(SO_4)_3,16H_2O$ crystallises out (Brauner). The double salts with sulphate of potassium are insoluble in a solution of K_2SO_4. Lustrous needles of the *acid salt*, $La_2(SO_4)_3,H_2SO_4$, separate out from the solution of the sulphate in sulphuric acid (Brauner). The crystals of the nitrate have the composition $La(NO_3)_3,6H_2O$. Its double salt, $La(NO_3)_3,2NH_4NO_3,4H_2O$, is important for the separation of lanthanum and forms large colourless crystals. The salts: $LaPO_4$, $La_2(CO_3)_3,8H_2O$, $LaCl_3,PtCl_4,13H_2O$, $La_2[Pt(CN)_4]_3,18H_2O$, &c., have also been studied.

The carbide, LaC_2, is obtained, by heating the oxide with carbon in the electric furnace, as a crystalline mass, which is decomposed by water, like the carbide of yttrium. The spectrum of the spark of chloride of lanthanum is very bright and contains many lines, and gives the possibility of detecting the presence of even small traces of lanthanum.

Cerium, Ce = 140·2 (Brauner).—The element was obtained in a metallic state by the action of sodium upon $CeCl_3$. Mozander obtained it as a grey powder, Wohler in globules. Winkler obtained not entirely pure cerium from Ce_2O_4 by means of magnesium. Pure metallic cerium was obtained by Norton and Hillebrand, by the electrolysis of fused $CeCl_3$, as an iron-grey metal of sp. gr. 6·628: it melts with greater ease than silver, is malleable and ductile, and can be drawn into wires when hot. It keeps well in dry air, becomes coated with oxide in damp air, and burns brightly at a high temperature. It emits sparks when scratched with a file or flint. It enters into reaction with the halogen acids and water like La. A hydride, Ce_2H_4(?), is formed by heating the oxide with magnesium in a stream of hydrogen. As already mentioned, cerium forms two basic oxides and one peroxide. Ce_2O_3 is a more energetic base than CeO_2 or Ce_2O_4.

A. *Compounds of the type* CeX_3.—The lower oxide, Ce_2O_3, is not really known in a free state, but a hydroxide, $Ce(OH)_3$, is obtained by precipitating solutions of RX_3 with caustic potash or soda as a white voluminous precipitate, which absorbs oxygen from the air, and first turns lilac-coloured (a hydrate of Ce_2O_3,Ce_2O_4 is formed) and then yellow owing to the formation of $Ce(OH)_4$. The corresponding salts, RX_3, are colourless and have no absorption spectra. They are sweet and astringent to the taste. The chloride, $CeCl_3$, is obtained by heating the oxide in the vapour of CCl_4, and also as a sublimate by burning metallic cerium in a stream of chlorine. A hydrate, $2CeCl_3,15H_2O$, crystallises out from a solution of the hydroxide or carbonate in hydrochloric acid. This hydrate is perhaps the same as that obtained by the action of gaseous hydrochloric acid on $CeCl_3,7H_2O$. The sulphide, Ce_2S_3, is obtained (like La_2S_3) by burning metallic cerium in the vapours of sulphur or by heating the oxide in hydrogen sulphide. It is a dark-brown amorphous mass. Golden yellow scales of the sulphide are formed by fusing the oxide with sodium pentasulphide and lixivating with water. The anhydrous sulphate, $Ce_2(SO_4)_3$, is obtained by heating the hydrated salt to 440°. It is readily soluble in ice-cold water, and crystallises from its solutions at the ordinary temperature as a *hydrate*, $Ce_2(SO_4)_3,8H_2O$, in rhombic octahedra, and not in the monoclinic system like the octahydrated salts of the other earths. Alcohol precipitates the same octahydrated salt from aqueous solutions. Besides this, sulphate of cerium forms hydrates with $5H_2O$, $6H_2O$, $9H_2O$ (isomorphous with the lanthanum salt) and $12H_2O$. The double salt, $3K_2SO_4,Ce_2(SO_4)_3$, is insoluble in a solution of K_2SO_4. A difficultly soluble double salt, $Na_2SO_4,Ce(NO_3)_3,6H_2O$, is also known, which forms very deliquescent crystals. With NH_4NO_3, it gives a salt, $Ce(NO_3)_3,2NH_4NO_3,4H_2O$, which is isomorphous with the salt of lanthanum. The phosphate, $CePO_4$, is the chief constituent of the mineral monazite. The salts, $Ce_2(CO_3)_3,5H_2O$, platinichlorides, $2(CeCl_3PtCl_4),27H_2O$, and $2(CeCl_3,2PtCl_4),21H_2O$, $Ce[Pt(CN)_5]_2,9H_2O$, &c., are also known. The *formate*, $Ce(CHO_2)_3$, and *oxalate*, $Ce_2(C_2O_4)_3,11H_2O$, are only slightly soluble. The *carbide*, CeC_2, is obtained by heating the oxide CeO_2 with carbon in the electric furnace

(Moissan), and is a reddish-yellow, transparent, crystalline substance. With water it gives a mixture containing 75 per cent. of acetylene and some ethylene, methane, and smaller amounts of solid and liquid hydrocarbons. If there be less carbon than is required to form the carbide, an oxycarbide, $CeC_2,2CeO_2$, is formed in reddish-brown plates. The composition of the carbide of cerium is the same as those of Al and Th.

B. *Compounds of the type* CeX_4.—The *higher oxide*, CeO_2 or Ce_2O_4, is obtained by igniting the oxalate, sulphate, nitrate, and other salts as an almost white powder, possessing a slight yellow tint and having the sp. gr. 6·74. It is insoluble in all acids except strong sulphuric acid. It gives colourless regular octahedra when fused with NaCl (sp. gr. 7·3) or borax—sp. gr. 7·4—or K_2SO_4—sp. gr. 8·0—which are insoluble in any acid. The *hydrate*, $2CeO_2,3H_2O$, is obtained by reacting with chlorine on $Ce(OH)_3$ and shaking up with KHO. The hydroxides, $Ce(OH)_4$ and $CeO(OH)_2$, are also known. The corresponding salts, RX_4, are yellow or brown, and have strong oxidising properties. *Tetrachloride of cerium*, $CeCl_4$, is not known in a pure state. It is evidently present in the brown solution obtained by dissolving $Ce(OH)_4$ in cold hydrochloric acid. The solution of the hydroxide in methyl alcohol containing hydrochloric acid is more stable. When treated with carbonate of potassium or ammonium it gives very unstable double salts in the form of yellow crystals. Pure double salts of the composition R_2CeCl_6 have been obtained with salts of organic bases, such as pyridine, quinoline, and triethylamine (Coppel). *Tetrafluoride of cerium*, CeF_4,H_2O, is formed by treating $Ce(OH)_4$ with hydrofluoric acid. It loses water when heated, and at a higher temperature evolves a gas containing free fluorine. A double salt has been obtained with fluoride of potassium, $3KF,2CeF_4,2H_2O$ (Brauner). The *sulphate* of the higher oxide of cerium, $Ce(SO_4)_2,4H_2O$, is easily obtained by dissolving $Ce(OH)_4$ in dilute sulphuric acid and forms yellow crystals. When CeO_2 is dissolved in hot sulphuric acid, it forms also the sulphate of the trioxide, and the two combine to give a double salt, $Ce_2(SO_4)_3,Ce_2(SO_4)_4,24H_2O$, in the form of brown hexagonal crystals. These crystals may also be obtained from the two component salts by synthesis, and the salt $Ce_2(SO_4)_3$ may be replaced by the salts of La, Pr, Nd, &c. (Brauner). The nitrate, $Ce(NO_3)_4$, is unknown in a pure state, and its solution is easily decomposed by water. With the nitrates of the alkali metals it forms double salts of the type $R_2Ce(NO_3)_6 (R = NH_4, K, Rb, Cs)$. The salts of Mg, Zn, Ni, Co, Mn contain $8H_2O$.

Peroxide of cerium, CeO_3.—Its hydroxide is obtained as a precipitate, like $Fe(OH)_3$, by the addition of H_2O_2 and ammonia to the salts of the lower oxides. When boiled with water it passes into $Ce(OH)_4$. The peroxide is soluble in $KHCO_3$ and crystallises from the solution as a double salt, $Ce_2O_3(CO_3)_3,4K_2CO_3,12H_2O$, in blood-red crystals (Job).

Praseodymium, Pr, 140·95 (Brauner).—This element has been obtained as a grey powder by the action of magnesium on the oxide. It forms a hydride with hydrogen and a nitride with nitrogen (Matignon).

Praseodymium gives two forms of oxides: Pr_2O_3 and Pr_2O_4 and compounds of them, Pr_4O_7 and $Pr_{10}O_{18}$, and also a hydroxide of the peroxide Pr_2O_5. (a) *The oxide* Pr_2O_3. When the oxalate or sulphate is strongly ignited it gives the intermediate oxide, $Pr_{10}O_{18}$, which, when strongly ignited in a stream of hydrogen, forms the oxide Pr_2O_3 as a beautiful light-green powder [of sp. gr. 7·07. Pr_2O_3 is readily soluble in acids, and forms bright light-green salts, which give a characteristic absorption spectrum. Praseodymium chloride, $PrCl_3$, is obtained by heating the oxalate in a stream of HCl gas, as a beautiful green crystalline mass which is only slightly volatile when heated (Brauner). The *hydrate*, $PrCl_3,7H_2O$, crystallises out in deliquescent crystals from a solution of the oxide in hydrochloric acid. The sulphide, Pr_2S_3, is obtained by heating the sulphate in hydrogen sulphide as a chocolate-coloured mass. The anhydrous sulphate, $Pr_2(SO_4)_3$, is easily dissolved in ice-cold water. The hydrate, $Pr_2(SO_4)_3,8H_2O$, crystallises out from the solution in monoclinic crystals, which are isomorphous with the sulphates of U, Nd, Sm, Tb, and Er. There are also hydrated sulphates with $5H_2O$ and $6H_2O$. The double salt, $Pr_2(SO_4)_3,3K_2SO_4,H_2O$, is insoluble in a solution of K_2SO_4. The *acid sulphate*, $3H_2SO_4,Pr_2(SO_4)_3$, is obtained by dissolving the neutral salt in warm sulphuric acid; on cooling it separates out in the form of lustrous green silky needles. The nitrate, $Pr(NO_3)_3,6H_2O$, forms deliquescent crystals. The double salt, $Pr(NO_3)_3,2NH_4NO_3,4H_2O$, crystallises in large crystals which deliquesce in moist air. This property is of great importance for separating praseodymium from the other rare earths. Besides these the following salts have been investigated and obtained: $Pr_2(CO_3)_3,8H_2O$, $PrCl_3,PtCl_4,12H_2O$, $Pr_2[Pt(CN)_4]_3,18H_2O$, the *acetate* $Pr(C_2H_3O_2)_3,2H_2O$, and the oxalate $Pr_2(C_2O_4)_3,11H_2O$. A *carbide of praseodymium*, PrC_2, was obtained by Moissan in the electric furnace from the oxide and carbon, and takes the form of yellow hexagonal plates. It evolves chiefly acetylene under the action of water. (b) The *dioxide*, PrO_2, is a brownish-black or black powder. It is obtained impure by burning the oxalate in oxygen or air at a red heat (Scheele). It may be obtained in a pure form by fusing the nitrate with nitre at 430° (Brauner): its sp. gr. is 5·98. It is converted into $Pr_{10}O_{18}(=2Pr_2O_3,3Pr_2O_4)$ when strongly heated. Although the higher oxide of praseodymium, PrO_2, like CeO_2, has its corresponding saline compounds of the type PrX_4, it is an 'ozone oxide,' for one of its oxygen atoms acts like the oxygen of peroxides. The salts of the type PrX_4 are very unstable; for instance, a solution of $PrCl_4$ rapidly decomposes into $PrCl_3$ and free chlorine. This instability is explained by the molecular volumes, the value for Pr_2O_4 being 57·9, and that for Pr_2O_3, 46·7, giving the very large difference of $+11{\cdot}2$ for 1 atom of oxygen. Hence the salts PrX_4 decompose with the evolution of oxygen and ozone. Pr_2O_4 converts CeX_3 into CeX_4, the salts of suboxide of manganese into those of the dioxide, and give a blue coloration with sulphate of strychnine and a 'catalytic' reduction with peroxide of hydrogen, $Pr_2O_4 + 3H_2SO_4 + H_2O_2 = Pr_2(SO_4)_3 + O_2 + 4H_2O$ (Brauner). A hydroxide of the *peroxide*, Pr_2O_5 is precipitated from the salts, PrX_3, by peroxide of hydrogen and alkalies. It is a pale-green gelatinous substance which rapidly decomposes with the evolution of oxygen.

Neodymium, $Nd = 143{\cdot}8$ (Brauner).—Praseodymium and neodymium are so alike that almost the only means of distinguishing them is by the colour of their salts and a few other physical properties. Also Pr_2O_3 is a somewhat stronger base than Nd_2O_3. A mixture of them, consisting of about $\frac{1}{3}$ Pr and $\frac{2}{3}$ Nd, was for a long time regarded as the element didymium, until Auër split it up into two component parts in 1885. Only a few pure compounds of neodymium are known. The corresponding element neodymium was obtained in the free state as a grey powder, by the action of magnesium upon Nd_2O_3. Neodymium forms three oxides, of which only the lowest one, Nd_2O_3, gives salts. (a) The *oxide* Nd_2O_3 is obtained by igniting the oxalate. It is a blue powder, readily soluble in acids, and forming beautifully tinted salts of a reddish-lilac or ruby-red colour. The absorption spectrum has more than 20 bands. The chloride, $NdCl_3$, is obtained as a rose-coloured crystalline mass by heating the hydroxide in a stream of HCl. The hydrate, $NdCl_3,6H_2O$, crystallises out from solutions in deliquescent crystals. Nd_2S_3 (obtained like Pr_2S_3) is olive-coloured. The *sulphate* is somewhat soluble in ice-cold water, and deposits a hydrate, $Nd_2(SO_4)_3,8H_2O$, in the form of ruby-red monoclinic crystals, which are isomorphous with the sulphates of Y, Pr, Sm, Tb, Er, and Yb. It forms sparingly soluble double salts with K_2SO_4 and Na_2SO_4, and with excess of sulphuric acid gives an acid salt, $Nd_2(SO_4)_3,3H_2SO_4$, in the form of bright rose-coloured silky needles. The *nitrate*, $Nd(NO_3)_3,6H_2O$, yields a double salt, $Nd(NO_3)_3,2NH_4NO_3,4H_2O$, with NH_4NO_3. This salt is more soluble in water than the corresponding praseodymium salt. The *carbide of neodymium*, NdC_2, forms yellow hexagonal plates. It gives the same hydrocarbons as PrC_2 under the action of water. (b) The *dioxide*, NdO_2, is formed as a light-brown powder by heating the oxalate or nitrate in oxygen. It does not form corresponding salts, but evolves oxygen when acted on by acids, yielding salts NdX_3. (c) The *peroxide*, Nd_2O_5, is obtained as a hydrate by the action of peroxide of hydrogen and alkalies on solutions of salts of neodymium. Like Pr it forms a basic acetate, $Nd_2O_3,(C_2H_3O_2)_3(OH),H_2O$.

Samarium, Sm = 148 (about).—Those compounds of samarium which were discovered by Lecoq in 1879 have not yet been freed from the compounds of europium, so that the oxide gave a somewhat high atomic weight, Sm = 150·8. The metal is not known in the free state. The *oxide*, Sm_2O_2, is white, and has the sp. gr. 8·35: it forms topaz-yellow salts, the solutions of which give a characteristic absorption spectrum. The chloride, $SmCl_3,6H_2O$, is deliquescent. The sulphate, $Sm_2(SO_4)_3$, is a yellowish-white powder, its hydrate crystallising in the form $Sm_2(SO_4)_3,8H_2O$. With K_2SO_4 and Na_2SO_4, it forms double salts which dissolve with difficulty. The *acid sulphate*, $Sm_2(SO_4)_3,3H_2SO_4$, forms golden-yellow needles. The *nitrate* has the composition $Sm(NO_3)_3,6H_2O$. Clève obtained a whole series of other salts of samarium; for instance, $2SmCl_3,2PtCl_4,21H_2O$, $Sm[Pt_3(CN)_9],18H_2O$, forming yellow prisms with a blue lustre, &c. The *carbide*, SmC_2, forms transparent yellow hexagonal crystals which are decomposed by water, with the evolution of hydrocarbons rich in acetylene. The oxide of samarium is a weaker base than Nd_2O_3.

Europium, Eu = 151 (about).—The salts of this element were obtained by Demarçay from the former samarium by crystallising the nitrates from a concentrated nitric acid solution, and also from the double salts $2R(NO_3)_3,3Mg(NO_3)_2,24H_2O$; its atomic weight and the spectrum of its chloride form the most characteristic properties of europium. The existence of this element was already suspected by Crookes and Lecoq de Boisbaudran.

Gadolinium, Gd = 156·4, was discovered by Marignac in 1880 as Y*a*. The solubility of its nitrate in concentrated nitric acid gives the best means, with other fractional methods, of separating this element. Gadolinium only forms one oxide, Gd_2O_3, which is a white powder, readily soluble in acids, having the sp. gr. 7·41 and the volume 49. The salts of the type GdX_3 are colourless and do not give any absorption spectrum. Benedicks investigated $GdCl_3,6H_2O$, forming crystals of the cubic system, $GdBr_3,6H_2O$ and $Gd(NO_3)_3$ with 5 and 6½ H_2O. The double nitrate with NH_4NO_3 occurs in deliquescent needles, like those of all the elements of the yttrium group. The *sulphate*, $Gd_2(SO_4)_3,8H_2O$, is isomorphous with $Y_2(SO_4)_3,8H_2O$, and yields the anhydrous salt, $Gd_2(SO_4)_3$, when heated to 130°. The double sulphate with K_2SO_4 is soluble in a solution of K_2SO_4. The following salts are also known: $GdCl_3,PtCl_4,10H_2O$, the reddish-green $2Gd(CN)_3,3Pt(CN)_2,18H_2O$, and the *oxalate* $Gd_2(C_2O_4)_3,10H_2O$.

Terbium, Tb = 148–159–163?—According to the researches of Mozander, Delafontaine, Marignac, Roscoe, Lecoq de Boisbaudran, Clève, and others, an earth exists which, when obtained by gently igniting the oxalate, turns dark-orange owing to the presence of the higher oxide, but which loses this coloration and turns white when reduced by hydrogen. It forms colourless salts which have no absorption spectrum. The sulphate, $Tb_2(SO_4)_3,8H_2O$, is isomorphous with the yttrium salt. The *double sulphate* with K_2SO_4, stands, as regards its solubility, between those of the cerite and yttrium earths, as also is the case with the formate. In fractionating the terbium earths Lecoq found that they give a characteristic rotation spectrum, and Roscoe and Schuster investigated and measured the spark spectrum of the chloride. But Hoffmann and Krüss, notwithstanding the most careful fractional subdivision, could not obtain an earth with a constant molecular weight.

Erbium, Er, **Holmium**, Ho, **Thulium**, Tu, **Dysprosium**, Dy.—None of the compounds of these elements have been obtained in a state of purity, and it is only known that their atomic weights lie approximately between 160 and 170. It has already been mentioned that Marignac separated ytterbium, giving colourless salts from the former oxide of erbium, obtained by Bar and Bunsen. The name of erbium was then left to denote the yttrium earth, which gives rose-coloured salts and a bright spectrum and a characteristic absorption spectrum. Clève showed in 1880 that true erbium is accompanied by two other earths, holmium and thulium, which are difficult to separate. Oxide of holmium or the element X which Soret had previously discovered, more closely resembles the yttrium earth, while thulium approaches nearer to oxide of ytterbium. Lecoq de Boisbaudran showed that still another oxide may be separated from oxide of holmium, namely, oxide of dysprosium, and Crookes finds that this is also a complex body. According to Clève the atomic weight of erbium is 166·3, that of holmium less than 165, and that of thulium, Tu, about 170·7. The researches of Hoffmann and Krüss (1893), who subjected mixtures of these earths to a thorough fractional separation, showed that the products obtained by the methods then in vogue contain elements with an atomic weight of approximately R = 166, and that the distinct spectra of erbium and holmium show that these earths *may be further split up into several very similar earths* by a method of fractional analysis. Of the compounds of the mixture known as erbium, the oxide, Er_2O_3, is rose-coloured, and has the sp. gr. 8·64; the sulphate, $Er_2(SO_4)_3,8H_2O$, forms rose-coloured monoclinic crystals isomorphous with those of the salt of yttrium. It gives a very soluble double salt with K_2SO_4. Besides these, $Er(NO_3)_3,5H_2O$ and $Er_2[Pt(CN)_4]_3,12H_2O$, which forms red prisms with a lilac and green lustre, are also known. A hydrate of the peroxide, Er_2O_5, is obtained by the action of peroxide of hydrogen and alkalies.

Ytterbium, Yb = 173 (Nilson and A. Clève).—The oxide of the former ytterbium discovered by Marignac in 1878 was split up by Nilson (1880) into the weaker basic oxide of scandium and the more energetic basic oxide of pure ytterbium. This is the weakest base of all the yttrium earths. The only known *oxide*, Yb_2O_3, is a white powder which dissolves slowly in cold acids and has the sp. gr. 9·18. The salts of ytterbium are colourless and have no absorption spectrum; alkalies precipitate a colourless hydroxide from their solutions. Aqueous solutions of ytterbia in hydrochloric acid give $YbCl_3,6H_2O$ when evaporated. When heated in a stream of HCl gas it gives YbOCl and not $YbCl_3$, like the more energetic basic earths of this group. $Yb_2(SO_4)_3,8H_2O$ is comparatively soluble in cold water and crystallises in large transparent prisms like the salt of yttrium. More dilute solutions are partially decomposed by water, like a salt of a weak base. $Yb(NO_3)_3$ crystallises with 3 and 4 H_2O. Nilson and Clève (1902) described many other neutral and basic salts, such as the carbonate, phosphate, &c. The oxalate, $Yb_2(C_2O_4)_3,10H_2O$, dissolves with greater ease than any of the analogous salts of the rare metals in a solution of ammonium oxalate and in dilute sulphuric acid. The spark spectrum is very rich in lines (Thalén).

As has already been stated, some chemists, and especially Crookes, Lecoq de Boisbaudran, and Demarçay, conclude from the spectra that there exist several other elements of the rare earths. The independent existence of the *decipium* of Delafontaine and the *victorium* of Crookes is, however, most doubtful. I consider the latter to be a mixture composed chiefly of yttrium and terbium, as there is no place for an element with an atomic weight R = 117 in the periodic system.

As regards the position of the group of rare earth elements which begins with Ce = 140 and ends with Yb = 173 in the periodic system, these elements and also cerium are difficult to arrange in this system in its present form. Brauner (*Journal of the Russian Physico-Chemical Society*, 1902, xxxiv. pp. 142–153) makes the proposition that, just as in the eighth group, four elements occupy one place in the system, so also the elements of the rare earths form a node or bands and occupy the position IV., 8 which was formerly occupied by cerium alone. Brauner therefore proposes to pass directly in the 8th series of the periodic system from Ce, &c., to Ta, and to give it the following form:—

Groups:	0	I	II	III	IV	V	VI	VII	VIII		
Series 8	Xe 128	Cs 133	Ba 137	La 139	Ce &c. 140–173	Ta 182	W 184	190	Os 191	Ir 193	Pt 1

Where:	Ce &c. = Ce	Pr	Nd	Sm	Eu	Gd	Tb	Ho	Er	Tu	Yb
„	140–173 = 140	141	144	148	151	156	163?	165?	166?	171?	173

The uses of the rare earths in the arts are very limited. The dioxide of cerium is added to the oxide of thorium (1 per cent. of CeO_2 to 99 of ThO_2) in order to render it more luminous for use in Welsbach burners. Besides this, CeO_2 is employed for staining glass yellow and for fining black aniline dye. The oxalate of the higher oxide of cerium is also being used in medicine. Didymium is employed for clearing glasses; and, lastly, the crude mixture of the cerite earths (obtained from monazite as a by-product in the preparation of nitrate of thorium) is used for making fusible glasses and in the manufacture of china.

B. BRAUNER.

PRAGUE : *September* 1902.

CHAPTER XVIII

SILICON AND THE OTHER ELEMENTS OF THE FOURTH GROUP

CARBON, which gives the compounds CH_4 and CO_2, belongs to the fourth group of elements. The nearest element to carbon is silicon, which forms the compounds SiH_4 and SiO_2; its relation to carbon is like that of aluminium to boron or that of phosphorus to nitrogen. As carbon composes the principal and most essential part of animal and vegetable substances, so is silicon almost an invariable component of the rocky formations of the earth's crust. Silicon hydride, SiH_4, like CH_4, has no acid properties, but silica, SiO_2, resembles carbonic anhydride in possessing feeble acid properties. In a free state silicon is as non-volatile and non-energetic a non-metal as carbon. The form and nature of the compounds of carbon and silicon are therefore very similar. In addition to this resemblance, silicon presents one exceedingly important distinction from carbon, its higher oxygen compound, namely, **silica**, silicon dioxide, or silicic anhydride, SiO_2 being a solid, non-volatile, and exceedingly infusible substance, very unlike carbonic anhydride, CO_2, which is a gas. This expresses the essential peculiarity of silicon. The cause of this distinction may be most probably sought for in the polymeric nature of the composition of silica as compared with that of carbonic anhydride. The molecule of carbonic anhydride has the composition CO_2, as is seen by the density of the gas. The molecular weight and vapour density of silica, were it volatile, would probably correspond with the formula SiO_2; but it might be imagined that it would correspond to a far higher molecular weight, Si_nO_{2n}, principally from the fact that SiH_4 is a gas like CH_4, and $SiCl_4$ is liquid and volatile, boiling at 57°—that is, even lower than CCl_4, which boils at 76°. In general, analogous compounds of silicon and carbon have nearly the same boiling-points if they are liquid and volatile.[1]

---

[1] Chloroform, $CHCl_3$, boils at 60°, and silicon chloroform, $SiHCl_3$, at 34°; silicon ethyl, $Si(C_2H_5)_4$, boils at about 150°, and its corresponding carbon compound, $C(C_2H_5)_4$, at about 120°; ethyl orthosilicate, $Si(OC_2H_5)_4$, boils at 160°, and ethyl orthocarbonate, $C(OC_2H_5)_4$, at 158°. The specific volumes in a liquid state—that is, those of the silicon compounds—are generally slightly greater than those of the carbon compounds; for example, the volumes of $CCl_4=94$, $SiCl_4=112$, $CHCl_3=81$, $SiHCl_3=82$, of $C(OC_2H_5)_4$

From this it might be expected that silicic anhydride, SiO_2, would be a gas like carbonic anhydride, whilst in reality silica is a hard non-volatile substance,[1a] so that it may with great certainty be considered that in this condition it is polymeric with SiO_2, as on polymerisation—for instance, when cyanogen passes into paracyanogen, or hydrocyanic acid into cyanuric acid (Chap. IX.)—very frequently gaseous or volatile substances change into solid, non-volatile, and physically denser and more complex substances.[2] We shall first make acquaintance with free silicon and its volatile compounds, as substances in which the analogy of silicon with carbon is shown, not only in a chemical, but also in a physical sense.[3]

$=186$, and $Si(OC_2H_5)_4=201$. The corresponding salts have also nearly equal specific volumes—for example, that of $CaCO_3$ is 87, and that of $CaSiO_3=41$. It is impossible to compare SiO_2 and CO_2, because their physical states are so widely different.

[1a] But silica fuses and volatilises (Moissan) in the electric furnace—at about 3000°—and is also partially volatile at the temperature attained in the flame of detonating gas (Cremer, 1892).

[2] A property of intercombination is observable in the atoms of carbon, and a faculty for intercombination, or polymerisation, is also seen in the unsaturated hydrocarbons and carbon compounds in general. In silicon a property of the same nature is found to be particularly developed in silica, SiO_2; but this is not the case with carbonic anhydride. The faculty of the molecules of silica for combining both with other molecules and among themselves is exhibited in the formation of most varied compounds with bases, in the formation of hydrates with a gradually decreasing proportion of water down to anhydrous silica, in the colloid nature of the hydrate (the molecules of colloids are always complex), in the formation of polymeric ethereal salts, and in many other properties which will be considered in the sequel. Having come to this conclusion as to the polymeric state of silica as long ago as 1850–1860, I have found it to be confirmed by all subsequent researches on the compounds of silica, and, if I mistake not, this view has now been very generally accepted.

[3] It was only after Gerhardt, and in general subsequently to the establishment of the true atomic weights of the elements (Chap. VII.), that a true idea of the atomic weight of silicon and of the composition of silica was arrived at from the fact that the molecules of $SiCl_4$, SiF_4, $Si(OC_2H_5)_4$, &c., never contain less than 28 parts of silicon.

The question of **the composition of silica** was long the subject of the most contradictory statements in the history of science. In the eighteenth century Pott, Bergmann, and Scheele distinguished silica from alumina and lime. In the beginning of the last century Smithson for the first time expressed the opinion that silica was an acid, and the minerals of rocks, salts of this acid. Berzelius determined the presence of oxygen in silica, 8 parts of oxygen being united with 7 of silicon. The composition of silica was first expressed as SiO (and for the sake of shortness S only was sometimes written instead). An investigation into the amount of silica present in crystalline minerals showed that the amount of oxygen in the bases bears a very varied proportion to the amount of oxygen in the silica, and that this ratio varies from 2 : 1 to 1 : 3. The ratio 1 : 1 is also met with, but the majority of such minerals are rare. Other more common minerals contain a larger proportion of silica, the ratio between the oxygen of the bases and the oxygen of the silica being equal to 1 : 2, or thereabouts; such are the augites, labradorites, oligoclase, talc, &c. The higher ratio 1 : 3 is known for a widely distributed series of natural silicates—for example, the felspars. Those silicates in which the amount of oxygen in the bases is equal to that in the silica are termed **monosilicates**; their general formula will be $(RO)_2SiO_2$ or $(R_2O_3)_2(SiO_2)_3$. Those in which the ratio of the oxygen is equal to 1 : 2 are termed **bisilicates**, and their general formula will be

Free **silicon** can be obtained in an amorphous or crystalline state. Amorphous silicon is produced, like aluminium, by decomposing sodium silicofluoride by means of sodium: $Na_2SiF_6+4Na=6NaF+Si$. By treating the mass thus obtained with water the sodium fluoride may be extracted and the residue will consist of brown, powdery silicon. In order to free it from any silica which might be formed, it is treated with hydrofluoric acid. The powder of amorphous silicon is not lustrous; when heated it easily ignites, but does not completely burn. It fuses when very strongly heated, and has then the appearance of carbon.[4]

$ROSiO_2$ or $R_2O_3(SiO_2)_3$. Those in which the ratio is 1 : 3 will be **trisilicates**, and their general formula $(RO)_2(SiO_2)_3$ or $(R_2O_3)_2(SiO_2)_9$.

In these formulæ the now established composition of SiO_2—that is, that in which the atom of $Si=28$—is employed. Berzelius, who made an accurate analysis of the composition of felspar, and recognised it as a trisilicate formed by the union of potassium oxide and alumina with silica, in just the same manner as the alums are formed by sulphuric acid, gave silica the same formula as sulphuric anhydride—that is, SiO_3. In this case the formula of felspar would be exactly similar to that of the alums—that is, $KAl(SiO_4)_2$, like the alums, $KAl(SO_4)_2$. If the composition of silica be represented as SiO_3, the atom of silicon must be recognised as equal to 42 (if $O=16$; or if $O=8$, as it was before taken to be, $Si=21$).

The former formulæ of silica, $SiO(Si=14)$, and $SiO_3(Si=42)$, were first changed into the present one, $SiO_2(Si=28)$, on the basis of the following arguments:—An excess of silica occurs in nature, and in silicious rocks free silica is generally found side by side with the silicates, and one is therefore led to the conclusion that it has formed acid salts. It would therefore be incorrect to consider the trisilicates as normal salts of silica, for they contain the largest proportion of silica; it is much better to admit another formula with a smaller proportion of oxygen for silica, and it then appears that the majority of minerals are normal or slightly basic salts, while some of the minerals abounding in nature contain an excess of silica—that is, belong to the order of acid salts.

At the present time, when there is a general method (Chap. VII.) for the determination of atomic weights, the volumes of the volatile compounds of silica show that its atomic weight is 28, so that silica is SiO_2. Thus, for example, the vapour density of silicon chloride with respect to air is, as Dumas showed (1862), 5·94, and hence with respect to hydrogen it is 85·5, and its molecular weight consequently 171 (instead of 170, as indicated by theory). This weight contains 28 parts of silicon and 142 parts of chlorine, and therefore the molecule of silicon chloride is $SiCl_4$. As two atoms of chlorine are equivalent to one of oxygen, the composition of silica will be SiO_2—that is, the same as stannic oxide, SnO_2, or titanic oxide, TiO_2, and the like, and also the same as carbonic and sulphurous anhydrides, CO_2 and SO_2. But silica bears but little physical resemblance to the latter compounds, whilst stannic and titanic oxides resemble silica both physically and chemically. They are non-volatile, crystalline, insoluble, colloidal, also form feeble acids like silica, &c., and they might therefore be expected to form analogous compounds, and be isomorphous with silica, as Marignac (1859) found to be actually the case. He obtained stannofluorides, for example, an easily soluble strontium salt, $SrSnF_6$, $2H_2O$, corresponding with the already long known silicofluorides, $MSiF_6$, such as $SrSiF_6$, $2H_2O$. These two salts are almost identical in crystalline form (monoclinic; angle of the prism, 83° for the former and 84° for the latter; inclination of the axes, 103° 46′ for the latter and 103° 30′ for the former), that is, they are isomorphous. We may here add that the specific volume of silica in a solid form is 22·6, and that of stannic oxide 21·5.

[4] A similar form of silicon is obtained by fusing SiO_2 with magnesium, when an alloy of Si and Mg is also formed (Gattermann). By heating magnesium in a stream of SiF_4,

Crystalline silicon is obtained in a similar way, but by substituting an excess of aluminium for the sodium: $3Na_2SiF_6+4Al=6NaF+4AlF_3+3Si$. The part of the aluminium remaining in the metallic state dissolves the silicon, and the latter separates on cooling in a crystalline form. The excess of aluminium is removed after the fusion by means of hydrochloric and hydrofluoric acids. Silica, SiO_2, is readily reduced by calcium carbide, CaC_2, in the electric furnace, silicon being formed as a molten mass. Silicon is also reduced at the high temperature of the blast furnace and enters into the composition of the pig iron owing to its ability to form alloys with iron like cast iron. The best silicon crystals are obtained from molten zinc; 15 parts of sodium silicofluoride are mixed with 20 parts of zinc and 4 parts of sodium, and the mixture is thrown into a strongly heated crucible, a layer of common salt being used to cover it; when the mass fuses it is stirred, cooled, treated with hydrochloric acid, and then washed with nitric acid. Like graphite and charcoal, silicon, especially when crystalline, does not in any way act on the above-mentioned acids. It forms black, very brilliant, regular octahedra having a specific gravity of 2·49; it is a bad conductor of electricity, and does not burn even in pure oxygen (but it does in gaseous fluorine). The only acid which acts on it is a mixture of hydrofluoric and nitric acids; but caustic alkalies dissolve in it like aluminium, with evolution of hydrogen, thus showing its acid character. In general, silicon strongly resists the action of reagents, as also do boron and carbon. Crystalline silicon was obtained in 1855 by Deville, and amorphous silicon in 1826 by Berzelius.[4a]

Silicon hydride, SiH_4, analogous to marsh gas, was obtained first of all in an impure state, mixed with hydrogen, by two methods: by the action of an alloy of silicon and magnesium on hydrochloric acid,[5] and

---

Warren (1888) obtained silicon and its alloy with magnesium. Winkler (1890) found that Mg_5Si_3 and Mg_2Si are formed when SiO_2 and Mg are heated together at lower temperatures, whilst at a high temperature Si only is formed.

[4a] It is very remarkable that silicon decomposes carbonic anhydride at a white heat, forming a white mass which, after being treated with potassium hydroxide and hydrofluoric acid, leaves a very stable yellow substance of the formula SiCO, which is formed according to the equation, $3Si+2CO_2=SiO_2+2SiCO$. It is also slowly formed when silicon is heated with carbonic oxide. It is not oxidised when heated in oxygen. A mixture of silicon and carbon when heated in nitrogen gives the compound Si_2C_2N, which is also very stable. On this basis Schützenberger recognises a group, C_2Si_2, which, like C, is capable of combining with O_2 and N, like C.

We may add that Troost and Hautefeuille, by heating amorphous silicon in the vapour of $SiCl_4$, obtained crystalline silicon, and probably at the same time lower compounds of Si and Cl were temporarily formed. In the vapour of $TiCl_4$ under the same conditions crystalline titanium is formed (Levy, 1892). Carbon is set free when fused potassium carbonate is heated with silica.

[5] This alloy, as Beketoff and Chirikoff showed, is easily obtained by directly heating finely divided silica (the experiment may be conducted in a test tube) with magnesium

by the action of the galvanic current on dilute sulphuric acid, using electrodes of aluminium containing silicon. In these cases silicon hydride is set free, together with hydrogen, and the presence of the hydride is shown by the fact that the hydrogen separated ignites spontaneously on coming into contact with the air, water and silica being formed. The formation of silicon hydride by the action of hydrochloric acid on magnesium silicide is perfectly akin to the formation of phosphoretted hydrogen by the action of hydrochloric acid on calcium phosphide, to the formation of hydrogen sulphide by the action of acids on many metallic sulphides, and to the formation of hydrocarbons by the action of hydrochloric acid on white cast iron. On heating silicon hydride—that is, on passing it through an incandescent tube—it is decomposed into silicon and hydrogen, just like the hydrocarbons; but the caustic alkalies, although without action on the latter, react with silicon hydride according to the equation: $SiH_4+2KHO+H_2O=SiK_2O_3+4H_2$.

Silicon chloride, $SiCl_4$, is obtained from amorphous anhydrous

powder (Chap. XIV., notes 17 and 18). The substance formed, when thrown into a solution of hydrochloric acid, evolves spontaneously inflammable and impure silicon hydride, so that the self-inflammability of the gas is easily demonstrated by this means.

In 1850–60 Wöhler and Buff obtained an alloy of silicon and magnesium by the action of sodium on a molten mixture of magnesium chloride, sodium silicofluoride, and sodium chloride. The sodium then simultaneously reduces the silicon and magnesium.

Friedel and Ladenburg subsequently prepared silicon hydride in a pure state, and showed that it is not spontaneously inflammable in air, at the ordinary pressure, but that, like PH_3, and like the mixture prepared by the above methods, it easily takes fire in air under a lower pressure or when mixed with hydrogen. They prepared the pure compound in the following manner: Wöhler showed that when dry hydrochloric acid gas is passed through a slightly heated tube containing silicon it forms a very volatile colourless liquid, which fumes strongly in air: this is a mixture of silicon chloride, $SiCl_4$, and **silicon chloroform,** $SiHCl_3$, which corresponds with ordinary chloroform, $CHCl_3$. This mixture is easily separated by distillation, because silicon chloride boils at 57°, and silicon chloroform at 36°. The formation of the latter will be understood from the equation, $Si+3HCl=H_2+SiHCl_3$. It is a colourless inflammable liquid of specific gravity 1·6. It forms a transition product between SiH_4 and $SiCl_4$, and may be obtained from silicon hydride by the action of chlorine and $SbCl_5$, and is itself also transformed into silicon chloride by the action of chlorine. Gattermann obtained $SiHCl_3$ by heating the mass obtained after the action (note 4) of Mg upon SiO_2, in a stream of chlorine (with HCl) at about 470°. Friedel and Ladenburg, by acting on anhydrous alcohol with silicon chloroform, obtained an ethereal compound having the composition $SiH(OC_2H_5)_3$. This ether boils at 136°, and when acted on by sodium disengages silicon hydride, and is converted into ethyl orthosilicate, $Si(OC_2H_5)_4$, according to the equation: $4SiH(OC_2H_5)_3=SiH_4+3Si(OC_2H_5)_4$ (the sodium seems to be unchanged), which is exactly similar to the decomposition of the lower oxides of phosphorus, with the evolution of phosphoretted hydrogen. If we designate the group C_2H_5 contained in the silicon ethers by Et, the parallel is found to be exact:

$$4PHO(OH)_2=PH_3+3PO(OH)_3;\quad 4SiH(OEt)_3=SiH_4+3Si(OEt)_4.$$

silica (made by igniting the hydrate) mixed with charcoal,[6] heated to a white heat in a stream of dry chlorine—that is, by that general method by which many other chloranhydrides having acid properties are obtained. It is also formed by heating silicon in a stream of dry chlorine gas. Silicon chloride is purified from free chlorine by distillation over metallic mercury. Free silicon forms the same substance when treated with dry chlorine. It is a volatile colourless liquid, which boils at 59° and has a specific gravity of 1·52. It fumes strongly in air, has a pungent smell, and in general has the characteristic properties of the acid chloranhydrides. It is completely decomposed by water, forming hydrochloric acid and silicic acid, according to the equation: $SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl$.[7]

---

[6] The amorphous silica is mixed with starch, dried, and then charred by heating the mixture in a closed crucible. A very intimate mixture of silica and charcoal is thus formed. In Chapter XI., note 13, we saw that elements like silicon disengage more heat with oxygen than with chlorine, and therefore their oxygen compounds cannot be directly decomposed by chlorine, but that this can be effected when the affinity of carbon for oxygen is utilised to aid the action. When the mass obtained by the action of Mg upon SiO_2 is heated to 300° in a current of chlorine, it readily yields $SiCl_4$ (Gattermann): besides which, two other compounds, corresponding to $SiCl_4$, are formed, namely: Si_2Cl_6, which boils at 145° and solidifies at $-1°$, and Si_3Cl_8, which boils at about 212°. These substances, which answer to corresponding carbon compounds (C_2H_6 and C_3H_8), act upon water and form corresponding oxygen compounds; for instance, $Si_2Cl_6 + 4H_2O = (SiO_2H)_2 + 6HCl$ gives the analogue of oxalic acid $(CO_2H)_2$. This substance is insoluble in water, decomposes under the action of friction and heat with an explosion, and should be called **silico-oxalic acid**, $Si_2H_2O_4$ (see note 11a).

[7] Silicon chloride shows a similar behaviour with alcohol. This is accompanied by a very characteristic phenomenon; on pouring silicon chloride into anhydrous alcohol a momentary evolution of heat is observed, owing to a reaction of double decomposition, but this is immediately followed by a powerful cooling effect, due to the disengagement of a large amount of hydrochloric acid—that is, there is an absorption of heat from the formation of gaseous hydrochloric acid. This is a very instructive example in this respect; here two processes, occurring simultaneously—one chemical and the other physical—are divided from each other by time, the latter process showing itself by a distinct fall in temperature. In the majority of cases the two processes proceed simultaneously, and we only observe the difference between the heat developed and absorbed. In acting on alcohol, silicon chloride forms **ethyl orthosilicate**, $SiCl_4 + 4HOC_2H_5 = 4HCl + Si(OC_2H_5)_4$. This substance boils at 160°, and has a specific gravity 0·94. Another salt, ethyl metasilicate, $SiO(OC_2H_5)_2$, is also formed by the action of silicon chloride on anhydrous alcohol: it volatilises above 300°, having a sp. gr. 1·08. It is exceedingly interesting that these two ethereal salts are both volatile, and both correspond with silica, SiO_2: the first ether corresponds to the hydrate $Si(OH)_4$, orthosilicic acid, and the second to the hydrate $SiO(OH)_2$, metasilicic acid. As the nature of hydrates may be judged from the composition of salts, so also, with equal right, can ethereal salts serve the same purpose. The composition of an ethereal salt corresponds with that of an acid in which the hydrogen is replaced by a hydrocarbon radicle—for instance, by C_2H_5. And, therefore, it may be truly said that there exist at least the two silicic acids above mentioned. We shall afterwards see that there are really several such hydrates; that these ethereal salts actually correspond with hydrates of silica is clearly shown from the fact that they are decomposed by water, and that in moist air they give alcohol and the corresponding hydrate, although the hydrate which is obtained in the

The most remarkable of the haloid compounds of silicon is **silicon fluoride**, SiF_4. It is a gaseous substance only liquefied by intense cold, −100°, and is obtained (Chap. XI.) directly by the action of hydrofluoric acid on silica and its compounds ($SiO_2 + 4HF = 2H_2O + SiF_4$), and also by heating fluor spar with silica ($2CaF_2 + 3SiO_2 = 2CaSiO_3 + SiF_4$).[8] In order to prepare silicon fluoride, sand or broken glass is mixed with an equal quantity by weight of fluor spar and 6 parts by weight of strong sulphuric acid, and the mixture gently heated. It fumes strongly in air, reacting with the aqueous vapours, although it is produced from silica and hydrofluoric acid with the separation of water. It is evident that a reverse reaction occurs here; that is to say, the water reacts with the silicon fluoride, but the reaction is not complete. This phenomenon is similar to that which occurs when water decomposes aluminium chloride, but at the same time hydrochloric acid dissolves aluminium hydroxide and forms the same aluminium chloride. The relative amount of water present (together with the temperature) determines the limit and direction of the reaction. The faculty which silicon fluoride has of reacting with water is so great that it takes up the elements of water from many substances—for instance, like sulphuric acid, it chars paper. Water dissolves about 300 volumes of this gas, but in this case it is not a common dissolution which takes place, but a reaction. During the first absorption of silicon fluoride by water, silicic acid is separated in the form of a jelly, but a certain quantity of the silicon fluoride also remains in the liquid, because the hydrofluoric acid

---

residue always corresponds with the second ethereal salt only—that is, it has the composition $SiO(OH)_2$; this form corresponds also to carbonic acid in its ordinary salts. This hydrate is formed as a vitreous mass when the ethyl silicates are exposed to air, owing to the action of the atmospheric moisture on them. Its specific gravity is 1·77.

Silicon bromide, $SiBr_4$, and silicon bromoform, $SiHBr_3$, are substances closely resembling the chlorine compounds in their reactions, and they are obtained in the same manner. Silicon iodoform, $SiHI_3$, boils at about 220°, has a specific gravity of 8·4, reacts in the same manner as silicon chloroform, and is formed, together with silicon iodide, SiI_4, by the action of a mixture of hydrogen and hydriodic acid on heated silicon. **Silicon iodide** is a solid at the ordinary temperature, fusing at about 120°; it may be distilled in a stream of carbonic anhydride, but readily takes fire in air, and behaves with water and other reagents just like silicon chloride. It may be obtained by the direct action of the vapour of iodine on heated silicon. Besson (1891) also obtained $SiCl_3I$ (boils at 113°), $SiCl_2I_2$ (172°), and $SiClI_3$ (220°), and the corresponding bromine compounds. All the halogen compounds of Si are capable of absorbing 6 or more NH_3. Besides which Besson obtained $SiSCl_2$ by heating Si in the vapour of chloride of sulphur; this compound melts at 74°, boils at 185°, and gives with water the hydrate of SiO_2, HCl, and H_2S.

[8] This property of calcium fluoride of converting silica into a gas and a vitreous fusible slag of calcium silicate is frequently taken advantage of in the laboratory and in practice in order to remove silica. The same reaction is employed for preparing silicon fluoride on a large scale in the manufacture of hydrofluosilicic acid (see sequel).

formed dissolves the other part of the silica[9] and forms the so-called **hydrofluosilicic acid**: $H_2SiF_6 = SiF_4 + 2HF = SiH_2O_3 + 6HF - 3H_2O$, that is to say, a metasilicic acid, SiH_2O_3, in which O_3 is replaced by F_6. This view of the composition of hydrofluosilicic acid may be admitted, because it forms a whole series of crystallisable and well-defined salts. In general, the whole reaction of water on silicon fluoride may be expressed by the equation: $3SiF_4 + 3H_2O = SiO(OH)_2 + 2SiH_2F_6$. Hydrofluosilicic acid and silicic acid resemble each other as much, and differ as much, in their chemical character as water and hydrofluoric acid. For this reason silicic acid is a feebler acid than hydrofluosilicic acid, and in addition to this the former is insoluble, and the latter soluble, in water.[10] Hydrofluosilicic acid is also formed when silicic acid is dissolved in a solution of hydrofluoric acid. It is incapable of volatilising without decomposition, and on heating the concentrated acid, silicon fluoride is evolved, leaving an aqueous solution of hydrofluoric acid. This is the reason why solutions of hydrofluosilicic acid corrode glass. This decomposition may be further accelerated by the

---

[9] The amount of heat developed by the solution of silicic acid, SiO_2,nH_2O, in aqueous hydrofluoric acid, xHF,nH_2O, increases with the magnitude of x and normally equals $x5600$ heat units, where x varies between 1 and 8. However, when $x = 10$, the maximum amount of heat is developed ($=49,500$ units), and beyond that the amount decreases (Thomsen).

[10] In reality, however, it would seem that the reaction is still more complex, because the aqueous solution of silicon fluoride does not yield a hydrate of silica, but a fluohydrate (Schiff), $Si_2O_3(OH)F$, corresponding to the (pyro-) hydrate $Si_2O_3(OH)_2$, equal to $SiO(OH)_2,SiO_2$, so that the reaction of silicon fluoride on water is expressed by the equation: $5SiF_4 + 4H_2O = 3SiH_2F_6 + Si_2O_3(OH)F + HF$. However, Berzelius states that the hydrate, when well washed with water, contains no fluorine, which is probably due to the fact that an excess of water decomposes $Si_2O_3(OH)F$, forming hydrofluoric acid and the compound $Si_2O_3(OH)_2$. Water saturated with silicon fluoride disengages silicon fluoride and hydrofluoric acid when treated with hydrochloric acid, the gelatinous precipitate being simultaneously dissolved. It may be further remarked that hydrofluosilicic acid has been frequently regarded as $SiO_2,6HF$, because it is formed by the solution of silica in hydrofluoric acid, but only two of these six hydrogens are replaced by metals. On concentration, solutions of the acid begin to decompose when they reach a strength of $6H_2O$ per H_2SiF_6, and therefore the acid may be regarded as $Si(OH)_4,2H_2O,6HF$, but the corresponding salts contain less water, and there are even anhydrous salts, R_2SiF_6, so that the acid itself is most simply represented as H_2SiF_6.

If gaseous silicon fluoride be passed directly into water, the gas-conducting tube becomes clogged with the precipitated silicic acid. This is best prevented by immersing the end of the tube under mercury, and then pouring water over the mercury; the silicon fluoride then passes through the mercury, and only comes into contact with the water at its surface, and consequently the gas-conducting tube remains unobstructed. The silicic acid thus obtained soon settles, and a colourless solution with a pleasant but distinctly acid taste is procured.

Mackintosh, by taking 9 per cent. of hydrofluoric acid, observed that in the course of an hour its action on opal attained 77 per cent. of the possible amount, whilst the action on quartz during the same time did not exceed 1½ per cent. of its possible value. This shows the difference in structure of these two modifications of silica, which will be more fully described in the sequel.

addition of sulphuric acid, or even of other acids. Hydrofluosilicic acid, when acting on potassium and barium salts, gives precipitates, because the salts of these metals are but sparingly soluble in water: thus, $2KX + H_2SiF_6 = 2HX + K_2SiF_6$. The potassium salt is obtained in the form of very fine octahedra, but the precipitate does not form quickly, and at first appears as a jelly. Nevertheless, the decomposition is complete, and is taken advantage of for obtaining from salts of potassium their corresponding acids.[10a]

Silicon, having so much in common with carbon, is also able to combine with it in the proportion given by the law of substitution, that is, it forms a **carbide of silicon**, CSi, called **carborundum** and obtained by Mühlhäuser and Aitchison in the United States, and by Moissan in France (1891), and others, by reducing silica with carbon in the electric furnace at a temperature of about 2,500°,[11] i.e., by the action of an electric current upon a mixture of carbon and SiO_2 with NaCl. After treating the resultant mass with acids and washing with water, carborundum is obtained in transparent, lustrous grains of a greenish colour, possessing great hardness (greater than that of corundum) and therefore used for polishing the hardest kinds of steel and stones. The specific gravity is about 3·1. Carborundum does not alter at a red heat, does not burn, and apparently approaches the diamond in its properties. (In 1894 Moissan obtained a similar very hard compound for boron, B_6C, sp. gr. 2·5.)

According to the principle of substitution, if silicon forms SiH_4, a series of hydrates, or hydroxyl derivatives, ought to exist corresponding with this hydride. The first hydrate of an alcoholic character ought to have the composition $SiH_3(OH)$; the second hydrate, $SiH_2(OH)_2$; the third, $SiH(OH)_3$;[11a] and the last, $Si(OH)_4$. The last is a hydrate of

---

[10a] The sodium salt is far more soluble in water, and crystallises in the hexagonal system. The magnesium salt, $MgSiF_6$, and calcium salt are soluble in water. The salts of hydrofluosilicic acid may be obtained not only by the action of the acid on bases or by double decompositions, but also by the action of hydrofluoric acid on metallic silicates. Sulphuric acid decomposes them, with evolution of hydrofluoric acid and silicon fluoride, and the salts when heated evolve silicon fluoride, leaving a residue of metallic fluoride, R_2F_2.

[11] See note 4a. Probably, in his researches, Schützenberger had already obtained CSi together with other silicon compounds. An amorphous, less hard compound of the same alloy is also obtained together with the hard crystalline CSi.

[11a] The following consideration is very important in explaining the nature of the lower hydrates which are known for silicon. If we suppose water to be taken up from the first hydrates (just as formic acid is $CH(OH)_3$, *minus* water), we shall obtain the various lower hydrates corresponding with silicon hydride. When ignited they should, like phosphorous and hypophosphorous acids, disengage silicon hydride, and behind leave a residue of silica—i.e., of the oxide corresponding to the highest hydrate—just as organic hydrates (for example, formic acid with an alkali) form carbonic anhydride as the highest oxygen compound. Such imperfect hydrates of silicon, or, more correctly speaking, of

silica, because it is equal to $SiO_2 + 2H_2O$; and it is formed by the action of water on silicon chloride, when all four atoms of chlorine are replaced by four hydroxyl groups.

Silica or silicic anhydride, both in the free state and in combination with other oxides, enters into the composition of most of the rock formations of the earth's crust. These silicious compounds are substances varying so much in their properties, crystalline forms, and relations to one another that they are comprised (like the carbon compounds) in a special branch of natural science, and are treated of in works on mineralogy; so that, in dealing with them further, we shall only give a short description of these various compounds. It is first of all necessary to turn to the description of silica itself, especially as it is not infrequently met with in nature in a separate state, and often forms whole masses of rock formations called 'quartz.' In an anhydrous condition silica appears in the greatest variety of natural forms—sometimes in well-formed crystals, hexagonal prisms, terminated by hexagonal pyramids. If the crystals are colourless and transparent, they are called **rock crystal.** This is the purest form of silica. Prismatic crystals of rock crystal sometimes attain considerable size, and as they are remarkable for their resistance to change, great hardness, and high index of refraction, they are used for ornaments, seals, necklaces, spectacles, optical instruments, &c.[12] Rock crystal coloured with

---

silicon hydride, were first obtained by Wöhler (1863) and studied by Geuther (1865), (see note 6).

Leucone is a white hydrate of the composition $SiH(OH)_3$. It is obtained by slowly passing the vapour of silicon chloroform into cold water: $SiHCl_3 + 3H_2O = SiH(OH)_3 + 3HCl$. But this hydrate, like the corresponding one of phosphorus or carbon, does not remain in this state of hydration, but loses a portion of its water. The carbon hydrate of this nature, $CH(OH)_3$, loses water and forms formic acid, $CHO(OH)$; but the silicon hydrate loses a still greater proportion of water, $2SiH(OH)_3$, parting with $3H_2O$, and consequently leaving $Si_2H_2O_3$. This substance must be an anhydride; all the hydrogen previously in the form of hydroxyl has been disengaged, two remaining hydrogens being left from SiH_4. The other similar hydrate is also white, and has the composition Si_3H_2O (nearly). It may be regarded as the above white hydrate $+ SiO_2$. A yellow hydrate, known as **chryseone** (silicone), is obtained by the action of hydrochloric acid on an alloy of silicon and calcium: its composition is approximately $Si_6H_4O_3$. Most probably, however, chryseone has a more simple composition, and stands in the same relation to the hydrate $SiH_2(OH)_3$ as leucone does to the hydrate $SiH(OH)_3$, because this very simply expresses the transition of the first compound into the second with the loss of water, $SiH_2(OH)_2 - H_2 + H_2O = SiH(OH)_3$. When these lower hydrates are ignited without access of air, they are decomposed into hydrogen, silicon, and silica—that is, it may be supposed that they form silicon hydride (which decomposes into silicon and hydrogen) and silica (just as phosphorous and hypophosphorous acids give phosphoric acid and phosphoretted hydrogen). When ignited in air, they burn, forming silica. They are none of them acted on by acids, but when treated with alkalies evolve hydrogen and give silicates; for example, with leucone: $SiH_2O_3 + 4KHO = 2SiK_2O_3 + H_2O + 2H_2$. They have no acid properties.

[12] Two modifications of rock crystal are known. These are very easily distinguished

organic matter in contact with which it has been produced has a brown or greyish colour, and then bears the name of **cairngorm** or **smoky quartz**. In this form it has the same uses as rock crystal, especially as it is often found in large masses. The same mineral frequently occurs, especially in aqueous formations, coloured lilac-red or pink by manganese or iron oxides, and is then known as **amethyst.** When finely coloured the amethyst is used as a precious stone, but amethysts most frequently occur as small crystals in the cavities formed in other rocky formations, and especially in those formed in silica itself. A similar anhydrous silica is often found in transparent non-crystalline masses, having the same specific gravity as rock crystal itself (2·66). In this case it is called **quartz**. Sometimes it forms complete rock formations, but more often penetrates or is interspersed through other rock formations, together with other silicious compounds. Thus, in granite, quartz is mixed with felspar and similar substances. Sometimes the colouring of quartz is so considerable that it is hardly transparent even in thin sheets, but it is often found in transparent masses slightly coloured with various tints. The existence in nature of enormous masses of quartz proves that it resists the action of water. When water destroys rock formations, the silicious minerals which they contain are partly dissolved and partly transformed into clay, &c. But the quartz remains untouched, in the form of the grains in which it existed in the rocky formation; sometimes, when crushed, it is carried away by the water and deposited. This is the origin of **sand**. Naturally, sometimes other rocky substances which are not changed by water, or only slightly acted on by it, are found in sand; but as these latter are more or less changed by the continuous action of water, it is not unusual to find sand which consists almost entirely of pure quartz. Common sand is generally coloured yellow or reddish brown by foreign mineral matter, consisting principally of ferruginous minerals and clays. The purest or so-called quartz sand is, however, rarely found, and is recognised by the absence of colour, and also by the test that when shaken in water it does not form any turbidity, which shows the absence of clay; when fused with bases it forms a colourless glass, and on this

from each other by their relation to polarised light: one rotates the plane of polarisation to the right and the other to the left—in the one the hemihedral faces are to the right and in the other to the left. This opposite rotatory power is taken advantage of in the construction of polarisers. But accompanying this physical difference—which is naturally dependent on a certain difference in the distribution of the molecules—there is not only no observable difference in the chemical properties, but none even in the density of the mass. Perfectly pure rock crystal is a substance which is most invariable with respect to its specific gravity. The numerous and accurate determinations made by Steinheil on the specific gravity of rock crystal show that (if the crystal be free from flaws) it is very constant and equal to 2·66.

account is a valuable material for the manufacture of glass. Sands were formed at all periods of the earth's existence; the ancient ones, compressed by strata of more recent formation and permeated with various substances (deposited from the infiltrating water), are sometimes solidified into rock, called **sandstone**, composing, in some places, whole mountain chains, and serviceable as a most excellent building material, on account both of the slight change it undergoes under the influence of atmospheric agencies and of the facility with which it may be wrought from rock formations into immense regularly shaped flags—the latter property is due to the primary laminar structure of the sand formations deposited, as above mentioned, by water. Many grindstones and whetstones are made from such rocks.

Anhydrous silica, SiO_2, is known not only in the condition of rock crystal and quartz, having a specific gravity of 2·6, but also in a special form, having other chemical and physical properties. This variety of silica has a specific gravity of 2·2, and is formed by fusing rock crystal or heating silicic acid.[12a] Silicic acid, when heated to a dull red heat, parts entirely with the water it contains, and leaves an exceedingly fine amorphous mass of silica (easily levigated, but difficult to moisten); it is characterised by such excessive friability that, when lightly blown on, a large mass of it rises into the air like a cloud of dust. A mass of anhydrous silica may be poured in this way from one vessel to another like a liquid, and like the latter it takes a horizontal position in the vessel containing it.[13] Anhydrous silica, like quartz,[13a] does not fuse in the heat of a furnace, but it fuses in the oxyhydrogen flame to a colourless glassy mass exactly similar to that formed in the same way from rock crystal. In this condition silica has a specific gravity of 2·2.[13b]

[12a] Several other modifications are known as minute crystals. For example, there is a particular mineral first found in Styria and known as **tridymite**. Its specific gravity, 2·3, and the form of its crystals clearly distinguish it from rock crystal; its hardness is the same as that of quartz—that is, below that of the ruby, but greater than that of felspar and glass.

[13] There is a distinct rise of temperature (about 4°) when amorphous silica is moistened with water. Benzene and amyl alcohol also give an observable rise of temperature. Charcoal and sand give the same result, although to a less extent.

[13a] Silica fused in the oxyhydrogen flame can be drawn into the finest threads (Boys) which are employed for supporting magnets and in physical apparatus dependent on torsion.

[13b] Silica also occurs in nature in two modifications. The opal and tripoli (infusorial earth) have a specific gravity of about 2·2, and are comparatively easily soluble in alkalies and hydrofluoric acid. Chalcedony and flint (tinted quartzose concretions of aqueous origin), agate and similar forms of silica of undoubted aqueous origin, although still containing a certain amount of water, have a specific gravity of 2·6, and correspond with quartz in the difficulty with which they dissolve. This form of silica sometimes permeates the cellulose of wood, forming one of the ordinary kinds of petrified wood. The silica may be extracted from it by the action of hydrofluoric acid, and the cellulose remains behind, clearly showing that silica in a soluble form (see sequel) has permeated

Both forms of silica are insoluble in ordinary acids, and even when they are in the state of powder, alkalies in solution act very slowly and feebly on them; rock crystal offers much greater resistance to the action of alkalies than the powder obtained by heating the hydrate. The latter is quite soluble, although but slowly, in hot alkaline solutions. This last property appertains in a greater degree to anhydrous silica having a specific gravity of 2·2 than to that which has a specific gravity of 2·6. Hydrofluoric acid more easily transforms the former into silicon fluoride than it does the latter. Both varieties of silica, when taken in the form of powder, combine readily with bases, forming, on being fused with an alkali, a vitreous slag, which is a salt corresponding with silica. Glass is such a salt, formed of alkalies and alkaline earthy bases; if the glass does not contain any of the latter—that is, if only alkaline glass is taken—a mass soluble in water is obtained. In order to obtain such **soluble glass**, potassium or sodium carbonate, or, better, a mixture of the two (fusion mixture), is fused with fine sand. A still better and further saturation of the alkalies with silica is effected by the action of alkaline solutions on the silicon hydrate met with in nature; for instance, an alkaline solution is often made use of to act on the so-called **tripoli**, or collection of silicious skeletons of the lowest microscopical infusoria, which is sometimes found in considerable layers in the form of a sandy mass. Tripoli is used for polishing, not only on account of the considerable hardness of the silica, but also because the microscopic bodies of the infusoria have a pointed shape, which, however, is not angular, so that they do not scratch metals like sand.[14] The alkaline solutions of silica obtained by boiling tripoli with caustic soda under pressure contain various proportions of silica and alkali.[14a] In order that it may contain the greatest

---

into the cells, where it has deposited the hydrate, which has lost water, and given a silica of sp. gr. 2·6. The quartzose stalactites found in certain caves are also evidently of a similar aqueous origin; their sp. gr. is also 2·6. As crystals of amethyst are frequently found among chalcedonies, and as Friedau and Sarrau (1879) obtained crystals of rock crystal by heating soluble glass with an excess of hydrate of silica in a closed vessel, there is no doubt but that rock crystal itself is formed in the wet way from the gelatinous hydrate. Chroustchoff obtained it directly from soluble silica. Thus, this hydrate is able to form not only the variety having the specific gravity 2·2, but also the more stable one of sp. gr. 2·6; and both exist with a small proportion of water and in a perfectly anhydrous state in an amorphous and crystalline form. All these facts are expressed by recognising silica as dimorphous, and their cause must apparently be looked for in a difference in the degree of polymerisation.

[14] Deposits of perfectly white tripoli have been discovered near Batoum, and might prove of some commericial importance; it is sometimes called kieselguhr.

[14a] Alkaline solutions, saturated with silica and known as **soluble glass**, are prepared on a large scale for technical purposes by fusing sand with alkaline carbonates and boiling the resultant glass (crushed) in boilers with water, or by the action of potassium (or sodium) hydroxide in a steam boiler on tripoli or infusorial earth, which contains a large proportion of amorphous silica. All solutions of the alkaline silicates

amount of silica, silicic acid should be added to the heated solution. Silicic acid is formed by taking any solution containing silica and alkali, and adding to it, by degrees, some acid—for instance, sulphuric or hydrochloric. If the experiment be carried on carefully and the solution be concentrated, the whole mass will thicken to a jelly, due to the gelatinous form of the **silicic acid** separated from the salt by the action of the acid. The decomposition may be expressed by the following equation : $SiNa_2O_3 + H_2O + 2HCl = 2NaCl + Si(OH)_4$. The hydrate separated, $Si(OH)_4$, easily loses part of the water and forms a jelly, the whole mass gelatinising if the solution is strong enough.[15]

---

have an alkaline reaction, and are even decomposed by carbonic acid. They are chiefly used by the dyer, for the same purposes as sodium aluminate, and also for giving a hardness and polish to stucco and other cements, and in general to substances which contain lime. A lump of chalk when immersed in soluble glass, or, better still, when moistened with a solution and afterwards washed in water (or, better, in hydrofluosilicic acid, in order to bind together the free alkali and make it insoluble), becomes exceedingly hard, loses its friability, is rendered cohesive, and cannot be levigated in water. This transformation is due to the fact that the hydrate of silica present in the solution acts upon the lime, forming a stony mass of calcium silicate, while the carbonic acid previously in combination with the lime enters into combination with the alkali and is washed away by the water.

[15] The equation given above does not express the actual reaction, for in the first place silica has the faculty of forming compounds with bases, and therefore the formula $SiNa_4O_4$ is only a particular case, if one may so express oneself. And, in the second place, silica gives several hydrates. In consequence of this, the hydrate precipitated does not actually contain so high a proportion of water as $Si(OH)_4$, but always less. The insoluble gelatinous hydrate which separates out is able (before, but not after, having been dried) to dissolve in a solution of sodium carbonate. When dried in air its composition corresponds with that of the ordinary salts of carbonic acid—that is, SiH_2O_3, or $SiO(OH)_2$. If gradually heated it loses water by degrees, and, in so doing, gives various degrees of combination with it. The existence of these degrees of hydration, having the composition $SiH_2O_3,nSiO_2$, or, in general, $nSiO_2,mH_2O$, where $m<n$, must be recognised, because most varied degrees of combination of silica with bases are known. The hydrate of silica, when not dried above 30°, has a composition of nearly $H_4Si_3O_8 = (H_2SiO_3)_2SiO_2$, but at 60° contains a greater proportion of silica—that is, it loses still more water; and at 100° a hydrate of the composition $SiH_2O_3,2SiO_2$, and at 250° one having approximately the composition $SiH_2O_3,7SiO_2$ are obtained.

These data show the complexity of the molecules of anhydrous silica. In the natural hydrates, the decrement of water proceeds quite consecutively, and, so to say, imperceptibly, until n becomes incomparably greater than m, and when the ratio becomes very large, anhydrous silica of the two modifications 2·6 and 2·2 is obtained. Even the composition $(SiO_2)_{10},H_2O$ corresponds with 2·9 per cent. of water, and natural hydrates often contain still less water than this. Thus some opals are known which contain only 1 per cent. of water, whilst others contain 7 and even 10 per cent. As the artificially prepared gelatinous hydrate of silica when dried has many of the properties of native opals, and as this hydrate always loses water easily and continually, there can be no doubt that the transition of $(SiO_2)_n(H_2O)_m$ into anhydrous silica, both amorphous and crystalline, is accomplished gradually. This can only be the case if the magnitude of n be considerable, and therefore the molecule of silica in the hydrate is undoubtedly complex, and hence the anhydrous silica of sp. gr. 2·2 and 2·6 does not contain SiO_2, but a complex molecule, Si_nO_{2n}—that is, the structure of silica is polymeric and complex, and not simple as represented above by the formula SiO_2.

Neither of the two varieties of anhydrous silica, nor the various natural gelatinous hydrates, are directly soluble in water. There is, however, a form of silica (or its hydrosol) known as soluble silica. Silica occurs in this state in nature. Small quantities of soluble silica are met with in all waters. Certain mineral springs, and especially hot springs—of which the best known are the Geysers of Iceland and those in the North American National Park (Yellowstone Valley)—contain a considerable amount of silica in solution. Such water, permeating the objects it meets with—for instance, **wood**—penetrates into them and deposits silica inside them, that is, transforms them into a **petrified** condition. Silicious stalactites, and also many (if not all) forms of silica are formed by such water. The absorption of silica by plants by means of their roots, and also by the lower organisms having silicious bodies, is due also to their nourishing themselves with the solutions containing silica which are continually formed in nature. In the straws of the grasses, in hard shave-grass, and especially in the knots of bamboo and other strawlike plants, a considerable quantity of silica is deposited, which must previously have been absorbed by the plants.

Silicic acid is a colloid. The gelatinous silicon hydrate is its hydrogel and the soluble hydrate the hydrosol (Chap. XII.). Both varieties may be easily obtained from the alkaline silicates and from water-glass. The very same substances—that is, aqueous solutions of soluble glass and acid—taken in the same proportion, may produce either the gelatinous or the soluble hydrate of silica, according to the way these solutions are mixed together. If the *acid be added* little by little *to the alkaline silicate*, with continuous stirring, a moment arrives when the whole mass thickens to a jelly—the hydrogel; in this case the silicic acid is formed in the alkaline solution and becomes insoluble. But if the mixing is done in the reverse order—that is, if the soluble glass *is added to the acid*, or if a quantity of acid is rapidly poured into the solution of the salt—then the separation of the silica takes place in the acid liquid, and it is obtained in the form of the soluble hydrate, the hydrosol.[16]

The hydrosol of silica prepared by mixing an excess of hydrochloric

---

[16] The presence of an excess of acid aids the retention of the silica in the solution, because the gelatinous silica obtained in the above manner is more soluble in water containing acid than in pure water. This would seem to indicate a feeble tendency of silica to combine with acids, and it might even have been imagined that in such a solution the hydrate of silica is held in combination by an excess of acid, had Graham not obtained soluble silica perfectly free from acid, and if there were not solutions of silica free from any acid in nature. At all events a tolerably strong solution of free silica or silicic acid may be obtained from soluble glass diluted with water.

acid with a solution of sodium silicate may be freed from the admixtures of both hydrochloric acid and salt, sodium chloride, **by means of dialysis**,[17] as **Graham** showed (in 1861) in inquiring into the nature of colloids (Chap. I.), and making many other important chemical investigations. The solution, containing the acid, salt, and silica, all dissolved in water, is poured into a dialyser—that is, a vessel with a porous diaphragm surrounded by water. Certain substances pass more easily than others through the diaphragm. This may be represented thus: the passage through the diaphragm proceeds in both directions, and if the solutions on each side of the diaphragm be equally strong, there will be equal numbers of molecules of the soluble substance passing into either side in a given time, some passing quickly and others slowly. The metallic chlorides and hydrochloric acid belong to the series of crystalloids which pass easily through a diaphragm, and therefore the hydrochloric acid and sodium chloride contained in the above-mentioned dialyser pass from the solution through the diaphragm into the water of the external vessel with considerable rapidity. The aqueous solution of colloidal silica also penetrates through the diaphragm, but very much more slowly. But if the amount of the dissolved substance is not the same on both sides of the diaphragm, the whole system strives to attain a state of equilibrium; that is, the given substance penetrates through the diaphragm from the side where it is in excess to the part where there is a smaller quantity of it. All substances which are soluble in water have the faculty of penetrating through a membrane swollen in water, but the velocities of penetration are not equal, so that the dialyser separates substances like a sieve. The silica passes less rapidly through the diaphragm than the sodium chloride and hydrochloric acid, so that by repeatedly changing the external water it is easy to effect the extraction of the chlorine compounds from the dialyser, which will finally only contain a solution of silica. This extraction (of HCl and NaCl) may be so complete that the liquid taken from the dialyser will not give any precipitate with a solution of silver nitrate. Graham obtained in this way soluble silica having a distinctly acid reaction, which, however, disappeared on the addition of a very minute quantity of alkali; for ten parts of silica in the solution it was sufficient to take one part of alkali in order to give the liquid an alkaline reaction, so slightly energetic are the acid properties of silicic acid. The solution of silica obtained by this method becomes gelatinous on standing, on being heated, or on evaporation under the

---

[17] See Chap. I., note 18. A solution of water-glass mixed with an excess of hydrochloric acid is poured into the dialyser, and the outer vessel is filled with water, which is continually renewed. The water carries off the sodium chloride and hydrochloric acid, and the hydrosol remains in the dialyser.

receiver of an air-pump, &c. The hydrosol is transformed into the hydrogel, the soluble hydrate into the gelatinous.

Thus in addition to the gelatinous form of silicic acid, there exists also a variety of this substance, soluble in water, as is the case with alumina. Such variation in properties and exactly the same relations with regard to water characterise an immense series of other substances having a great significance in nature. Such substances are especially numerous among organic compounds, and particularly in those classes which compose the principal material of the bodies of animals and plants. It is sufficient to mention, for instance, the gelatin which is familiar to all as carpenter's and other glues, and in the form of size and jelly. The same substance is also known in the solution which is used to join objects together. In a peculiar insoluble condition it enters into the composition of hides and bones. These various forms of gelatin differ in the same way as the different varieties of silica. The property of forming a jelly is exactly the same as in silica, and the adhesiveness of the solutions of both substances is identical; soluble silica adheres like a solution of gelatin. The same properties are again shown by starch, rosin, albumin, and a number of similar substances. The diaphragms used in dialysis are also insoluble, gelatinous forms of colloids. The bodies of animals and plants consist largely of similar matter, insoluble in water, corresponding with the gelatinous or insoluble silicon hydrate, or with glue. The albumin which coagulates when eggs are boiled is a typical form of the gelatinous condition of such substances in the body. These few indications are sufficient to show how great is the significance of those transformations which are so well marked in silica. The facts, discovered by Graham in 1861–1864, comprise the most essential acquisitions in the general association of these phenomena of nature in the history of organic forms. The facility of transition from hydrogel to hydrosol is the first condition of the possibility of the development of organisms. The blood contains hydrosols, and the hydrogels of the same substances are contained in the muscles and tissues, and especially on the surface, of the body. All tissues are formed from the blood, and in that case the hydrosols are converted into hydrogels.[18] The absence of crystallisation

---

[18] A similar process occurs in plants. For example, when they secrete a store of material for the following year in their bulbs, roots, &c. (for instance, the potato in its tubers), the solutions from the leaves and stems penetrate the roots and other parts in the form of hydrosols, where they are converted into hydrogels, that is, into an insoluble form, which is acted on with difficulty and is easily kept unaltered until the period of growth—generally the following spring—when they are reconverted into hydrosols, and the insoluble substance re-enters the sap, and serves as a source of the hydrogels in the leaves and other portions of plants.

and the property of passing, apparently under the influence of feeble agencies, from the soluble condition to the insoluble, gelatinous condition, constitute the fundamental properties of all colloids.[19]

Silica, by its ability **to form salts**, stands, in the series of oxides, on the boundary line, and occupies, with regard to the acids, just such a place as alumina occupies on the side of the bases—that is, aluminium hydroxide is the representative of the feeblest bases, and silicic acid is the least energetic of acids (at least in the presence of water—that is, in aqueous solutions); in alumina, however, the basic properties are distinctly expressed, whilst in silica the acid properties preponderate. Like all feeble acid oxides it is capable of forming, with other acids, saline compounds which are but slightly stable and are very easily decomposed in the presence of water. The chief peculiarity of the silicates consists in the number of their types. The salts formed with nitric or sulphuric acid exist in one, two, or three tolerably stable forms, but for acids like silicic acid the number of forms is very great—indeed, almost unlimited. The natural silicates in particular furnish proof of this fact; they contain various bases in combination with silica, and for one and the same base there often exist various degrees of combination. As feeble bases are capable of forming basic salts—that is, compounds of a normal salt with a feeble base (either the hydroxide or the oxide)—in addition to normal ones, so the feeble acid oxides (although not all) form, in addition to normal salts, highly acid salts—that is, normal salts *plus* acid (hydrate or anhydride). Such are boric, phosphoric, molybdic, chromic, and especially silicic, acids.

In order to explain these relations it is necessary first to recollect the existence of the various hydrates of silica, or silicic acids,[20] and then

---

[19] As regards their chemical composition the colloids are very complex—that is, they have a high molecular weight and a large molecular volume—in consequence of which they do not penetrate through membranes, and are readily subject to variation in their physical and chemical properties (owing to their complex structure and polymerism?). They have but little chemical energy, and are generally feeble acids, if belonging to the order of oxides or hydrates, such as the hydrates of molybdic and tungstic acids (Chap. XXI.). But now the number of substances capable, like colloids, of passing into aqueous solutions and of easily separating out from them, as well as of appearing in an insoluble form, must be supplemented by various other substances, among which soluble gold and silver (Chap. XXIV.) and other metals are of particular interest. So that now it may be said that the capacity of forming colloid solutions is not limited to a definite class of compounds, but is, if not a general, at all events an exceedingly widely distributed phenomenon. Colloids may be regarded as a kind of transition stage between liquids and solids. Tammann's researches (see Physical Chemistry) on the effect of pressure lead to this conclusion.

[20] This is in accordance with the generally accepted representation of the relations between salts and the hydrates of acids, but it is of little help in the study of silicious compounds. Generally speaking, it becomes necessary to explain the power of $(SiO_2)_n$ to combine with $(RO)_m$, where n may be greater than m, and where R may be

to turn our attention to the similarity between silicon compounds and metallic alloys. Silica is an oxide having the appearance of, and in many respects the same properties as, those oxides which combine with it, and if two metals are capable of forming homogeneous alloys in which there exist definite or indefinite compounds, it is permissible to assume a similar power of forming alloys in the case of analogous oxides. Such alloys are found in indefinite amorphous masses in the form of glass, lava, slags, and a number of similar silicious compounds which do not contain any definite types of combination, but nevertheless are homogeneous throughout their mass. By slow cooling, or under other circumstances, definite crystalline compounds may—and sometimes do—separate from this homogeneous mass, as also sometimes definite crystalline alloys separate from metallic alloys.

The formation of crystalline rocks in nature is partly of such a character. By aqueous or igneous agency, but in any case in a liquid condition, those oxides which form the earth's crust and its crystalline minerals came into mutual contact. First of all they formed a shapeless mass, of which lava, glass, slags, and solutions are examples ; and then certain definite compounds of oxides existing in this alloy or in the shapeless mass were formed. This is entirely similar to two metals forming a homogeneous alloy,[21] and under known circumstances

---

H_2,Ca, &c. Here we are aided by those facts which have been attained by the investigation of carbon compounds, especially with respect to glycol. Glycol is a compound having the composition $C_2H_6O_2$, only differing from alcohol, C_2H_6O, by an extra atom of oxygen. This hydrate contains two hydroxyl groups, which may be successively replaced by chlorine, &c. Hence the composition of glycol should be represented as $C_2H_4(OH)_2$. It has been found that glycol forms so-called polyglycols. Their origin will be understood from the fact that glycol as a hydrate has a corresponding anhydride of the composition C_2H_4O, known as ethylene oxide. This substance is ethane, C_2H_6, in which two hydrogens are replaced by one atom of oxygen. Ethylene oxide is not the only anhydride of glycol, although it is the simplest one, because $C_2H_4O = C_2H_4(OH)_2 - H_2O$. Various other anhydrides of glycol are possible, and have actually been obtained, of the composition $nC_2H_4(OH)_2 - (n-1)H_2O = (C_2H_4)_nO_{n-1}(OH)_2$. These imperfect anhydrides of glycol, or **polyglycols**, still contain hydroxyls like glycol itself, and therefore are of an alcoholic character in the same sense as glycol itself. They are obtained by various methods, and, amongst others, by the direct combination of ethylene oxide with glycol, because: $C_2H_4(OH)_2 + (n-1)C_2H_4O = (C_2H_4)_nO_{n-1}(OH)_2$. The most important circumstance, from a theoretical point of view, is that these polyglycols may be distilled without undergoing decomposition, and that the general formula given above expresses their actual molecular composition. Hence we have here a direct combination of the anhydride with the hydrate, and, moreover, a repeated one. The formula A,nH_2O may be used to express the composition of glycol and polyglycols with respect to ethylene oxide in the most simple manner, if A stand for ethylene oxide. When $n = 1$ we have glycol, when n is greater than 1 a polyglycol. Such also is the relationship of the salts of hydrate of silica, if A stand for silica, and if we imagine also that H_2O may be taken m times. Such a representation of the **polysilicic acids** corresponds with that of the polymerism of silica.

[21] For us the latter have not a saline character only because they are not regarded from this point of view, but an alloy of sodium and zinc is, in a broad sense, a salt in many

(for instance, on cooling the alloy, or, in the case of aqueous solution, when the two metals are simultaneously liberated from the solution), definite crystalline compounds are separated. In any case there is no doubt that there is less distinction between silica and bases, than between bases and such anhydrides; as, for instance, sulphuric or nitric, or even carbonic, as is seen on comparing the physical and chemical properties of silica and various kinds of oxides. Alumina, especially, is exceedingly near akin to silica; not only in the hydrated state, but also in the anhydrous condition, there exists a certain similarity between the crystalline forms of alumina and silica in the un-

of its reactions, for it is subject to the same double decompositions as sodium phosphide or sulphide, which clearly have saline properties. The latter (sodium phosphide), when heated with ethyl iodide, forms ethyl phosphide, and the former—i.e., the alloy of zinc and sodium—gives zinc ethyl; that is, the element (P, S, Zn) which was united with the sodium passes into combination with the ethyl: $RNa + EtI = REt + NaI$. By combining sodium successively with chlorine, sulphur, phosphorus, arsenic, antimony, tin, and zinc, we obtain substances having less and less the ordinary appearance of salts, but if the alloy of sodium and zinc cannot be termed a salt, then perhaps this name cannot be given to sodium sulphide, or to the compounds of sodium with phosphorus. The following circumstance may also be observed: with chlorine, sodium gives only one compound (with oxygen, at the most three), with sulphur five, with phosphorus probably still more, with antimony naturally still more, and the more analogous an element is to sodium, the more varied are the proportions in which it is able to combine with it, the less are the alterations in the properties brought about by the combination, and the nearer does the compound formed approach to the class of compounds known as indefinite chemical compounds. In this sense a silicious alloy, containing silica and other acids, is a salt. To a certain extent the oxide plays the same part as the sodium, whilst the silica plays the part of the acid element which was taken up successively by zinc, phosphorus, sulphur, &c., in the above examples. Such a comparison of the silica compounds with alloys presents the great advantage of including under one category the definite and indefinite silica compounds—that is, brings under one head such crystalline substances as certain minerals, and such amorphous substances as are frequently met with in nature, and are artificially prepared; for example, glass, slags, enamels, &c.

If the compounds of silica are substances like the metallic alloys, then (1) the chemical union between the oxides of which they are composed must be a feeble one, as it is in all compounds formed between analogous substances. In reality such feeble agencies as water and carbonic acid are able, although slowly, to act on and destroy the majority of the complex silica compounds in rocks, as we have already seen; (2) their formation, like that of alloys, should not be accompanied by a considerable alteration of volume; and this is actually the case. For example, felspar has a specific gravity of about 2·6, and therefore, taking its composition to be $K_2O,Al_2O_3,6SiO_2$, we find its volume, corresponding with this formula, to be $556{\cdot}8 : 2{\cdot}6 = 214$, the volume of $K_2O = 35$, that of $Al_2O_3 = 26$, and that of $SiO_2 = 22{\cdot}6$. Hence the sum of the volumes of the component oxides, $35 + 26 + 6 \times 22{\cdot}6 = 196$, which is very nearly equal to that of the felspar, so that the formation of the latter is attended by a slight expansion, and not by contraction, as happens in the majority of other cases when combinations determined by strong affinities are accomplished. In the case in question the same phenomenon is observed as in solutions and alloys—that is, as in cases of feeble affinities. So also the specific gravity of glass is directly dependent on the amount of those oxides which enter into its composition. If in the preceding example we take the sp. gr. of silica to be, not 2·65, but 2·2, its volume becomes 27·3, and the sum of the volumes will be 224—that is, greater than that of orthoclase.

combined state. Both are very hard, transparent, inactive, non-volatile, infusible, and crystallise in the hexagonal system; in a word, they are remarkably similar, and for this reason they are capable, like two kindred metals, of entering into many different degrees of combination.

Isomorphous mixtures—differing by the substitution of oxides akin both in their physical and chemical characters—are very frequently met with among minerals, and the study of the latter gave the principal impetus to the study of isomorphism. Thus, in a whole series of minerals, lime and magnesia are found in variable and interchangeable proportions. Exactly the same may be said of potassium and sodium, of alumina and ferric oxide, of manganous, ferrous, magnesium oxides, &c. Such isomorphism does not, however, extend without change of form and properties beyond certain rather narrow limits.[22]

[22] It is, however, easy to imagine, and experience confirms the supposition, that in a complex silicious compound containing, for instance, sodium and calcium, the whole of the sodium may be replaced by potassium, and *at the same time* the whole of the calcium by magnesium, because then the substitution of potassium for the sodium will produce a change in the nature of the substance contrary to that which will occur owing to the calcium being replaced by magnesium. That increase in weight, decrease in density, increase of chemical energy, which accompanies the exchange of sodium for potassium will, so to speak, be compensated by the exchange of calcium for magnesium, because both in weight and in properties the sum of $Na + Ca$ is very near to the sum of $K + Mg$. *Pyroxene* or *augite* can be taken as an example; its composition may be expressed by the formula $CaMgSi_2O_6$; that is, it corresponds with the acid H_2SiO_3, and is a bisilicate. In many respects it closely resembles another mineral called *spodumene* (both being monoclinic). This latter has the composition $Li_6Al_8Si_{15}O_{45}$. On reducing both formulæ to an equal content of silica the following distinction will be observed between them: spodumene, $(Li_2O)_6(Al_2O_3)_8,30SiO_2$; augite, $(CaO)_{15}(MgO)_{15},30SiO_2$. That is, the difference between them consists in the sum of the magnesia and lime $(MgO)_{15} + (CaO)_{15}$ replacing the sum of the lithium oxide and alumina $(Li_2O)_6 + (Al_2O_3)_8$; and in the chemical relation these sums are near to one another, because magnesium and calcium, both in forms of oxidation and in energy (as bases), in all respects occupy a position intermediate between lithium and aluminium, and therefore the sum of the first may be replaced by the sum of the second.

If we take the composition of spodumene to be, as it is often represented, $Li_2O,Al_2O_3,4SiO_2$, the corresponding formula of augite will be $(CaO)_2,(MgO)_2,4SiO_2$, and also the amount of oxygen in the sum of Li_2O and Al_2O_3 will be the same as in $(CaO)_2$ and $(MgO)_2$. I may remark, for the sake of clearness, that lithium belongs to the first, aluminium to the third group, and calcium and magnesium to the intermediate second group; lithium, like calcium, belongs to the even series, and magnesium and aluminium to the uneven.

The representation of the substitutions of analogous compounds here introduced (D. Mendeléeff, 1856) finds confirmation in the facts relating, for example, to the tourmalins. Wülfing (1888), on the basis of a number of analyses (especially those by Röggs), states that all varieties contain an isomorphous mixture of alkali and magnesia tourmalins; into the composition of the former there enters $12SiO_2,3B_2O_3,8Al_2O_3,2Na_2O,4H_2O$, and of the latter $12SiO_2,3B_2O_3,5Al_2O_3,12MgO,3H_2O$. Hence it is seen that the former contains the sum of $3Al_2O_3,2Na_2O,H_2O$, which is replaced in the latter by $12MgO$, in which there is as much oxygen as in the sum of the more clearly defined base $2Na_2O$, the less basic $3Al_2O_3$ and H_2O—that is, the relation is here just the same as between augite and spodumene.

What I mean by this is that lime is not always replaced totally, but often only in small quantities, by magnesia, or by manganous and ferrous oxides, without changing the crystalline form. The same may be observed with regard to potassium and lithium, which may be in part, but not completely, replaced by sodium. On the total substitution of one metal for another, the entire nature of the substance is often (although not invariably) changed; for instance, *enstatite* (or bronzite) is a magnesium bisilicate with a small isomorphous substitution of calcium for magnesium; its composition is expressed by the formula $MgSiO_3$, and it belongs to the rhombic system. On complete substitution of calcium for magnesium, *wollastonite*, $CaSiO_3$, of the monoclinic system, is obtained; when manganese is substituted, *rhodonite*, of the triclinic system, is produced; but in all of them the angles of the prism are between 86° and 88°.[23]

---

[23] With respect to the silica compounds of the various oxides, it must be observed that only the **alkali salts** are known in a soluble form; all the others exist only in an insoluble form, so that a solution of the alkali compounds of silica, or soluble glass, gives a precipitate with a solution of the salts of the majority of other metals, and this precipitate will contain the silica compounds of the other bases. The maximum amount of the gelatinous hydrate of silica, which dissolves in caustic potash, corresponds with the formation of a compound, $2K_2O,9SiO_2$. But this compound is partially decomposed, with the precipitation of hydrate of silica on cooling the solution. Solutions containing a smaller amount of silica may be kept for an indefinite time without decomposing, and silica does not separate out from the solution; but such compounds crystallise from the solutions with difficulty. However, a crystalline bisilicate (with water) has been obtained for sodium having the composition Na_2O,SiO_2—i.e., corresponding to sodium carbonate. The whole of the carbonic acid is evolved, and a similar soluble sodium metasilicate is obtained on fusing 3·5 parts of sodium carbonate with 2 parts of silica. If less silica is taken, a portion of the sodium carbonate remains undecomposed; however, a substance may then be obtained of the composition $Si(ONa)_4$, corresponding with orthosilicic acid. It contains the maximum amount of sodium oxide capable of combining with silica on fusion. It is a sodium orthosilicate, $(Na_2O)_2,SiO_2$.

Calcium carbonate, and the carbonates of the alkaline earths in general, also evolve all their carbonic acid when heated with silica, and in some instances even form somewhat fusible compounds. Lime forms a fusible slag of **calcium silicate**, of the compositions CaO,SiO_2 and $2CaO,SiO_2$. With a larger proportion of silica the slags are infusible in a furnace. The magnesium **slags** are less fusible than those containing lime, and are often formed in smelting metals. Many compounds of the metals of the alkaline earths with silica are also met with in nature. For instance, among the magnesium compounds there is **olivine** $(MgO)_2,SiO_2$, sp. gr. 3·4, which occurs in meteorites, and sometimes forms a precious stone (peridote), and is found also in slags and basalts. It is decomposed by acids, is infusible before the blowpipe, and crystallises in the rhombic system. **Serpentine**, $3MgO,2SiO_2,2H_2O$, sometimes forms whole mountains, and is distinguished for its great cohesiveness, being used therefore in the arts. It is generally tinted green, its specific gravity is 2·5, and it is exceedingly infusible, even before the blowpipe. It is acted on by acids. Among the magnesium compounds of silica, **talc** is very frequently met with in rocks and sometimes in compact masses; it can be used for writing like a slate pencil or chalk; and, being greasy to the touch, is also known as *steatite*. It crystallises in the rhombic system, and resembles mica in many respects; like it, it is divisible into laminæ, greasy to the touch, and has a sp. gr. 2·7. These laminæ are

The most remarkable complex silicious compounds are the **felspars**, which enter into nearly all the primary rocks like porphyry, granite, gneiss, &c. These felspars always contain silica, alumina, and oxides presenting marked basic properties, such as potash, soda, and lime. Thus the *orthoclase* (adularia), or ordinary felspar (monoclinic) of the granites, contains $K_2O,Al_2O_3,6SiO_2$; *albite* contains the same substances, only with Na_2O instead of K_2O (and belongs to the triclinic system); *anorthite* contains lime, its composition being $CaO,Al_2O_3,2SiO_2$. On expressing the last two as containing equal quantities of oxygen, we have :—

Albite	Na_2	Al_2	Si_6	O_{16}
Anorthite	Ca_2	Al_4	Si_4	O_{16}

It is then evident that, on the conversion of albite into anorthite, Na_2Si_2 is replaced by Ca_2Al_2, and this sum, both in chemical energy and in the form of oxide, may be considered as corresponding with the first, because sodium and silicon are extreme elements in chemical character (from groups I. and IV.), and calcium and aluminium are means between them (from groups II. and III.), and actually both these felspar minerals are not only of one (triclinic) system, but form (Tschermak, Schuster) all possible kinds of definite compounds (isomorphous mixtures) among themseves, as indicated by their composition and all their properties. Thus oligoclase, andesine, labradorite, &c. (plagioclases) are nothing more than mutual combinations of albite and anorthite. Labradorite consists of albite, in combination with from 1 to 2 molecules of anorthite. The class of **zeolites** corresponds to the felspars; they are hydrated compounds of a similar composition to the felspars. Thus *natrolite* consists of $Na_2O,Al_2O_3,3SiO_2,2H_2O$, and *analcime* presents the same composition, but contains $4SiO_2$ instead of $3SiO_2$. In general, the felspars and zeolites contain $RO,Al_2O_3,nSiO_2$, where n varies considerably.[24]

very soft, lustrous, and transparent, and are infusible and insoluble in acids. The composition of talc approaches nearly to $6MgO,5SiO_2,2H_2O$.

Among the crystalline silicates the following minerals are known:—**Wollastonite** (tabular spar), which crystallises in the monoclinic system; sp. gr. 2·8; it is semi-transparent, difficultly fusible, decomposes by acids, and has the composition of a metasilicate, CaO,SiO_2. But isomorphous mixtures of calcium and magnesium silicates occur with particular frequency in nature. The **augites** (sp. gr. 3·3), diallages, hypersthenes, hornblendes (sp. gr. 3·1), amphiboles, common asbestos, and many similar minerals, sometimes forming the essential parts of entire rock formations, contain various relative proportions of the bisilicates of calcium and magnesium partially mixed with other metallic silicates, and generally anhydrous, or only containing a small amount of water. In the pyroxenes, as a rule, lime predominates, and in the amphiboles (also of the monoclinic system), magnesia. Details must be looked for in works upon mineralogy.

[24] The majority of the silicious minerals have now been obtained artificially under various conditions. Thus N. N. Sokoloff showed that slags very frequently contain

Such complex silicates are generally insoluble in water,[25] and if they undergo change in it, it is but very slowly, and more often only

---

peridote. Hautefeuille, Chroustchoff, Friedel, and Sarasin obtained felspar identical in all respects with the natural minerals. The details of the methods here employed must be looked for in special works on mineralogy; but, as an example, we will describe the method of preparation of felspar employed by Friedel and Sarasin (1881). From the fact that felspar gives up potassium silicate to water even at the ordinary temperature (Debray's experiments), they concluded that the felspar in granites had an aqueous origin (and this may be supposed to be the case from geological data); then, in the first place, its formation could not be accomplished except in the presence of an excess of potassium silicate solution. In order to render this argument clear I may mention, as an example, that carnallite is decomposed by water into easily soluble magnesium chloride and potassium chloride, and therefore if it is of aqueous origin it could not be formed otherwise than from a solution containing an excess of magnesium chloride, and, in the second place, from a strongly heated solution; again, felspar itself and its fellow-components in granites are anhydrous. On these facts were based experiments of heating hydrates of silica with alumina and a solution of potassium silicate in a closed vessel. The mixture was placed in a sealed platinum tube, which was enclosed in a steel tube and heated to dull redness. When the mixture contained an excess of silica the residue contained many crystals of rock crystal and tridymite, together with a powder of felspar, which formed the main product of the reaction when the proportion of hydrate of silica was decreased, and a mixture of a solution of potassium silicate with alumina precipitated together with the silica by mixing soluble glass with aluminium chloride was employed. The composition, properties, and forms of the resultant felspar proved it to be identical with that found in nature. The experiments approach very nearly to the natural conditions, all the more so since felspar and quartz are obtained together in one mixture, as they so often occur in nature.

[25] The application of **cements** is based on this principle: they are those sorts of 'hydraulic' lime which generally form a stony mass, which hardens, even under water, when mixed with sand and water.

The hydraulic properties of cements are due to their containing calcareous and silico-aluminous compounds capable of combining with water and forming hydrates, which are then unacted on by water. This is best proved, in the first place, by the fact that certain slags containing lime and silica, and obtained by fusion (for example, in blast-furnaces), solidify like cements when finely ground and mixed with water; and, in the second place, by the method now employed for the manufacture of artificial cements (formerly only peculiar and comparatively rare natural products were used). For this purpose a mixture of lime and clay is taken, containing about 25 per cent. of the latter; this mixture is then heated, not to fusion, but until both the carbonic anhydride and water contained in the clay are expelled. This mass when finely ground forms Portland cement, which hardens under water. The process of hardening is based on the formation of chemical compounds between the lime, silica, alumina, and water. These substances are also found combined together in various natural minerals—for example, in the zeolites, as we saw above. In all cases cement which has set contains a considerable amount of water, and its hardening is naturally due to hydration—that is, to the formation of compounds with water. Well-prepared and very finely ground cement hardens comparatively quickly (in several days, especially after being rammed down), with 8 parts (and even more) of coarse sand and with water, into a stony mass which is as hard and durable as many stones, and more so than bricks and limestone. Hence not only all maritime constructions (docks, ports, bridges, &c.), but also ordinary buildings, are made of Portland cement, and are distinguished for their great durability. A combination of ironwork (ties, girders) and cement (Monier) is particularly suitable for the construction of aqueducts, arches, reservoirs, &c. Arches and walls made of such cements may be much less thick than those built up of ordinary stone. Hence the production and use of cement increase rapidly from year to year. The origin of accurate data respecting takes place in the presence of carbonic acid. Some of the silicates which are insoluble in water are easily and directly decomposed by acids; for instance, the zeolites and those fused silicates which contain a large quantity of energetic bases such as lime. Many of the silicates, like glass,[26] are hardly changed by acids, particularly if they contain

cements is chiefly due to Vicat. In Russia Professor Schuliachenko has greatly aided the extension of accurate data concerning Portland cement. Many works for the manufacture of cement have already been established in various parts of Russia, and this industry promises a great future in the arts of construction.

[26] **Glass** presents a complex composition similar to that of many minerals. The ordinary sorts of white glass contain about 75 per cent. of silica, 13 of sodium oxide, and 12 of lime; but some sorts of glass contain as much as 10 per cent. of alumina. The mixtures which are used for the manufacture of glass are also most varied. For example, about 300 parts of pure sand, 100 of sodium carbonate, and 50 of limestone are taken, and sometimes double the proportion of the latter. Ordinary **soda-glass** contains sodium oxide, lime, and silica as the chief component parts. It is generally prepared from sodium sulphate mixed with charcoal, silica, and lime (Chap. XII.), in which case the following reaction takes place at a high temperature: $Na_2SO_4 + C + SiO_2 = Na_2SiO_3 + SO_2 + CO$. Sometimes potassium carbonate is taken for the preparation of the better qualities of glass. In this case a glass, **potash-glass**, is obtained containing potassium oxide instead of sodium oxide. Tho best-known of these glasses is the so-called Bohemian glass or crystal, which is prepared by the fusion of 50 parts of potassium carbonate, 15 parts of lime, and 100 parts of quartz. The preceding kinds of glass contain lime, whilst crystal glass contains lead oxide instead. Flint glass—that is, the lead glass used for optical instruments—is prepared in this manner, naturally from the purest possible materials. *Crystal-glass*—i.e., glass containing lead oxide—is softer than ordinary glass, more fusible, and has a higher index of refraction. Borax is sometimes added to glass to render it more fusible, and suboxide of thallium to increase the index of refraction (especially in paste). However, although the materials for the preparation of glass may be most carefully sorted, a certain amount of iron oxides gets into the glass and renders it greenish. This coloration may be destroyed by adding to the vitreous mass one of a number of substances which are able to convert the ferrous oxide into ferric oxide; for example, manganese peroxide (because the peroxide is deoxidised to manganous oxide, which only gives a pale violet tint to the glass) and arsenious anhydride, which is deoxidised to arsenic, and this is volatilised. The manufacture of glass is carried on in furnaces giving a very high temperature (often in regenerator furnaces, Chap. IX.). Large stone or clay crucibles are placed in these furnaces, and the mixture destined for the preparation of the glass, having been first roasted, is charged into the crucibles. The temperature of the furnace is then gradually raised. The process takes place in three separate stages. At first the mass intermixes and begins to react; then it fuses, evolves carbonic acid gas, and forms a molten mass; and, lastly, at the highest temperature, it becomes homogeneous and quite liquid, which is necessary for the ultimate elimination of the carbonic anhydride and solid impurities, which latter collect at the bottom of the crucible. Tho temperature is then lowered somewhat, and the glass is taken out on tubes and blown into objects of various shapes. In the manufacture of window-glass it is blown into large cylinders, which are then cut at the ends and across, and afterwards bent back in a furnace into the ordinary sheets. After being worked up, all glass objects have to be subjected to a slow cooling (*annealing*) in special furnaces, otherwise they are very brittle, as is seen in the so-called 'Rupert's drops,' formed by dropping molten glass into water; although these drops are very hard and preserve their form, they break up into a fine powder if a small piece be knocked off them, owing to the great internal strain. In the manufacture of mirrors and many massive objects the glass is cast and then ground and polished. Coloured glasses are made either by directly introducing into the glass itself various oxides, which give their

much silica, whilst fusion with alkalies leads to the formation of compounds rich in bases, after which acids decompose the alloys formed.[27]

According to the periodic law, the nearest analogues of silicon ought to be elements of the uneven series, because silicon, like sodium, magnesium, and aluminium, belongs to this series.[28] Immediately after silicon follows ekasilicon or **germanium**, Ge=72, whose properties were predicted (1871) before Winkler (1886) in Freiberg, Saxony (Chap. XV. § 5), discovered this element in a peculiar silver ore called *argyrodite*, Ag_6GeS_5.[29] Easily reduced from the oxide by heating with hydrogen and charcoal, and separated from its solutions by zinc,

---

characteristic tints, or else a thin layer of a coloured glass is laid on the surface of ordinary glass. Green glasses are formed by the oxides of chromium and copper, blue by cobalt oxide, violet by manganese oxide, and red glass by cuprous oxide and by the so-called purple of Cassius—i.e., a compound of gold and tin—which will be described later. A yellow coloration is obtained by means of the oxides of iron, silver, or antimony, and also by means of carbon, especially for the brown tints for certain kinds of bottle-glass.

From what has been said about glass, it will be understood that it is impossible to give a definite formula for it, because it is a non-crystalline or amorphous alloy of silicates; but such an alloy can only be formed within certain limits in the proportions between the component oxides. With a large proportion of silica the glass very easily becomes clouded when heated; with a considerable proportion of alkalies it is easily acted on by moisture, and becomes cloudy in time on exposure to the air; with a large proportion of lime it becomes infusible and opaque, owing to the formation of crystalline compounds in it; in a word, a certain proportion is practically attained among the component oxides in order that the glass formed may have suitable properties. Nevertheless, it may be well to remark that the composition of good sorts of glass approaches to the formula, $Na_2O,CaO,6SiO_2$.

The coefficient of cubical expansion of glass is nearly equal to that of platinum and iron, being approximately 0·000027. The specific heat of glass is nearly 0·18, and the specific gravity of common soda glass nearly 2·5, that of Bohemian glass 2·4, and that of bottle glass 2·7. Flint glass is much heaver than common glass, because it contains the heavier oxide of lead, its specific gravity being 2·9 to 3·2. Further details will be found in text-books of technology.

[27] It must be recollected that although acids seem to act only feebly on the majority of silicates, nevertheless a finely levigated powder of silicious compounds is acted on by strong acids, especially with the aid of heat, the basic oxides being taken up and gelatinous silica left behind. In this respect sulphuric acid heated to 200° with finely divided silicious compounds in a closed tube acts very energetically.

[28] Such elements as silicon, tin, and lead were only brought together under one common group by means of the periodic law, although the quadrivalency of tin and lead was known much earlier. Generally silicon was placed among the non-metals, and tin and lead among the metals.

[29] At first (February 1886) the want of material to work on, the absence of a spectrum in the Bunsen's flame, and the solubility of many of the compounds of germanium, presented difficulties in the researches of Professor Winkler, who, on analysing argyrodite by the usual method, obtained a constant loss of 7 per cent., and was thus led to search for a new element. The presence of arsenic and antimony in the accompanying minerals also impeded the separation of the new metal. After fusion with sulphur and sodium carbonate, argyrodite gives a solution of a sulphide which is precipitated by an *excess* of hydrochloric acid; germanium sulphide is soluble in ammonia and is then precipitated by hydrochloric acid, as a *white* precipitate, which is dissolved

metallic germanium proved to be greyish white, easily crystallisable (in octahedra), brittle, fusible (under a coating of fused borax) at about 900°, and easily oxidisable; the specific gravity$=5·469$, the atomic weight$=72·3$, and the specific heat$=0·076$,[30] as might be expected for this element according to the periodic law. The corresponding **germanium dioxide**, GeO_2, is a white powder having a specific gravity of 4·703 ; water, especially when boiling, dissolves this dioxide (1 part of GeO_2 requires for solution 247 parts of water at 20°, 95 parts at 100°). It forms soluble salts with alkalies and is but sparingly soluble in acids.[31] In a stream of chlorine the metal forms **germanium chloride**, $GeCl_4$, which boils at 86°, and has a specific gravity of 1·887 at 18° ; water decomposes it, forming the oxide. All these properties [32] of germanium, showing its analogy to silicon and tin, form a most beautiful demonstration of the truth of the periodic law.[33]

(or decomposed) by water. After being oxidised by nitric acid, dried and ignited germanium sulphide leaves the oxide GeO_2, which is reduced to the metal when ignited in a stream of hydrogen.

[30] G. Kobb determined the spectrum of germanium. The wave-lengths of the most distinct lines are given in Chap. XIII.

[31] If germanium or its sulphide is heated in a stream of hydrochloric acid, it forms a volatile liquid, boiling at 72°, which corresponds to germanium chloroform, $GeHCl_3$. It is decomposed by water, forming a basic salt of the hydrate of the suboxide, GeO, which acts as a powerful reducing agent in hydrochloric acid solution. After prolonged heating with a solution of NaHO in large excess (about 5NaHO per $GeHCl_3$), all the suboxide passes into the solution, which, on the one hand, resembles the alkaline solutions of the hydrates of ZnO, PbO, Al_2O_3, SiO_2, and, on the other, bears some analogy to sodium formate, $CHNaO_2$, which is equivalent to $CO + NaHO$, while the germanium solution is $GeO + NaHO$; and this solution (Hantzsch, 1902), after being saponified with ethyl aceto-acetate and treated carefully with sufficient HCl to saturate all the alkali, gives an acid solution of GeH_2O_2, which may be regarded as either germanoformic acid or as the hydrosol (colloid solution) of hydrated suboxide of germanium, GeO,H_2O.

Voegelen (1902) showed that if chloride of germanium is added to sulphuric acid acting on zinc, it is partially converted (like As and Sb) into a volatile (gaseous) *hydride*, which when heated deposits metallic germanium, like arseniuretted hydrogen, in a thin mirror-like layer, which is grey by reflected and reddish by transmitted light. Judging from its reaction with sulphur (under the action of light), it has the composition GeH_4, and the reaction proceeds according to the equation, $GeH_4 + S_4 = GeS_2 + 2H_2S$.

[32] Under certain circumstances germanium gives a blue coloration like that of ultramarine, as Winkler showed, which might have been expected from the analogy of germanium with silicon.

[33] Winkler expressed this in the following words (*Jour. f. prakt. Chemie*, 1886, **34**, 182–183): ' . . . es kann keinem Zweifel mehr unterliegen, dass das neue Element nichts Anderes, als das vor fünfzehn Jahren von *Mendeléeff* prognosticirte *Ekasilicium* ist.'

'Denn einen schlagenderen Beweis für die Richtigkeit der Lehre von der Periodicität der Elemente, als den, welchen die Verkörperung des bisher hypothetischen "Ekasiliciums" in sich schliesst, kann es kaum geben, und er bildet in Wahrheit mehr, als die blosse Bestätigung einer kühn aufgestellten Theorie, er bedeutet eine eminente Erweiterung des chemischen Gesichtfeldes, einen mächtigen Schritt in's Reich der Erkenntniss.'

The increase of atomic weight from silicon 28 to germanium 72 is 44—that is, about the same difference as there is in the atomic weights of chlorine and bromine; between germanium and its next analogue, **tin** (Sn=119), the difference is 47—that is, almost as much as the amount by which the atomic weight of iodine exceeds that of bromine.

Metallic tin is rarely met with in **nature**; it occurs in the veins of ancient formations, almost exclusively in the form of oxide, SnO_2, called **tin-stone.** The best known tin deposits are in Cornwall and in Malacca. In Russia, tin ores have been found in small quantities on the shores of Lake Ladoga, in Pitkarand. The crushed ore may easily be separated from the earthy matter accompanying it by washing on inclined tables, as the tin-stone has a specific gravity of 6·9, whilst the impurities are much lighter. **Tin oxide is very easily reduced** to metallic tin by heating with charcoal. For this reason tin was known in ancient times, and the Phœnicians brought it from England. Metallic tin is cast into ingots of considerable weight or into thin sticks or rods. Tin has a white colour, rather duller and more blue than that of silver. It fuses easily at 232°, and crystallises on cooling. Its specific gravity is 7·2. The crystalline structure of ordinary tin is noticed in bending tin rods, when a peculiar sound is heard, produced by the fracture of the particles of tin along the surfaces of crystalline structure.

When pure tin is cooled to a low temperature it splits up into separate crystals, the bond between the particles is lost, the tin assumes a grey colour, becomes less brilliant—in a word, its properties become changed, as was shown by Fritzsche. This depends on the different structure (allotropic, dimorphous) which the tin then acquires, and is particularly remarkable because it is effected by cold in a solid.[33a] If such grey tin is fused, or even simply heated above 20°, it becomes like ordinary tin, but is again changed when cooled. If tin is powdered (see further on; tin becomes very brittle at about 200° and may then be reduced to a powder in a mortar) and moistened with a solution of tin in hydrochloric acid, it passes from the ordinary form into the grey variety with comparative ease. The transition temperature lies at about 20° (Cohen and van Dyk), the grey variety being formed below and the ordinary one above this temperature; still the conversion from one into the other variety proceeds slowly at temperatures about $+20°$, but at $-40°$ or $-50°$ the grey tin is rapidly formed. Its specific gravity is generally below that of ordinary tin, and sometimes even as low as 5·8.[34]

[33a] Emilianoff (1890) states that in the cold of the Russian winter 30 out of 200 tin moulds for candles were spoilt through becoming quite brittle.

[34] The tin deposited by the electric current from solutions of $SnCl_2$ appears in

Tin is softer than silver or gold, and is only surpassed by lead in this respect. In addition to this it is very ductile, but its tenacity is very slight, so that wire made from it will bear but little strain. In consequence of its ductility it is easily worked, by forging and rolling into very thin sheets (tin foil), which are used for wrapping round many articles to preserve them from the action of moisture, &c. In this case, however, and in many others, lead is mixed with the tin, which, within certain limits, does not alter the ductility. Although so soft at the ordinary temperatures, tin becomes brittle at 200° before fusing. Tin powder may be easily obtained if the metal be fused and then stirred while cooling. At a white heat tin may be distilled, but with more difficulty than zinc. If molten tin comes into contact with oxygen, it oxidises, forming stannic oxide, SnO_2, and **its vapour burns** with a white flame. **At ordinary temperatures tin does not oxidise**, and this very important property of tin allows it to be applied in many cases for covering other metals to prevent their oxidising. This is termed **tinning**. Iron and copper are frequently tinned. Iron and steel sheets, coated with tin, bear the name of tin plate (for the most part made in England), and are used for numerous purposes.[34a]

Tin with copper forms **bronze**, an alloy which is most extensively used in the arts. Bronze has various colours and a variety of physical properties, according to the relative amount of copper and tin which it contains. With an excess of copper the alloy has a yellow colour ; the admixture of tin imparts considerable hardness and elasticity to the copper. An alloy containing 78 parts of copper and about 22 per cent. of tin is so elastic that it is used for casting bells, which naturally require a very elastic and hard alloy.[35] For casting

---

crystals of the cubic system, and has a specific gravity of 7·8, which is less than that of ordinary tin. The tin deposited by an electric current from a neutral solution of $SnCl_2$ readily oxidises and becomes coated with SnO (Vignon, 1889).

[34a] Tin plate is prepared by immersing iron sheets, previously thoroughly cleansed by acid and mechanical means, in molten tin. If after this the coating of tin be rapidly cooled—for instance, by dashing water over it—it crystallises in diverse star-shaped figures, which become visible when the sheets are first immersed in dilute aqua regia and then in a solution of caustic soda.

The coating of iron by tin guards it against the direct access of air, but it only preserves the iron from oxidation so long as it forms a perfectly continuous coating. If the iron is left bare in certain places, it will be powerfully oxidised at these spots, because the tin is electro-negative with respect to the iron, and thus the oxidation is confined entirely to the iron in the presence of tin. However, a dense and invariable alloy is formed over the surface of contact of the iron and tin, which binds the coating of tin to the remaining mass of the iron. Tin may be fused with cast iron. The coating of copper objects by tin is generally done to preserve the copper from the action of acid liquids, which would attack the copper in the presence of air and convert it into poisonous salts. Tin is not acted on in this manner, and therefore copper vessels for the preparation of food should be tinned.

[35] The ancient Chinese alloys containing about 20 per cent. of tin (specific gravity of

statues and various large or small ornamental articles alloys containing 2 to 5 per cent. of tin, 10 to 30 per cent. of zinc, and 65 to 85 per cent. of copper, are used.[36] Tin is also often used alloyed with lead, for making various objects—for instance, drinking vessels.

Tin decomposes the vapour of water when heated with it, liberating the hydrogen and forming stannic oxide. Sulphuric acid, diluted with

---

alloys about 8·9), which have been rapidly cooled, are distinguished for their resonance and elasticity. These alloys were formerly manufactured in large quantities in China for the musical instruments known as *tom-toms*. Owing to their hardness, alloys of this nature are also employed for casting guns, bearings, &c., and an alloy containing about 11 per cent. of tin is known as gun-metal. The addition of a small quantity of phosphorus, up to 2 per cent., renders bronze still harder and more elastic, and the alloy so formed is now used under the name of phosphor-bronze.

The alloy $SnCu_3$ (58·8 per cent. of Cu) is brittle, of a *bluish* colour, and has nothing in common with either copper or tin in its appearance or properties. It remains perfectly homogeneous on cooling, and acquires a crystalline structure (Riche). These signs clearly indicate that the alloy $SnCu_3$ is a product of chemical combination, which is also seen to be the case from its density—namely, 8·91, which is greater than that of copper. Had there been no contraction, the density of the alloy would be 8·21. It is the heaviest of all the alloys of tin and copper, the density of tin being 7·29 and that of copper 8·8. The alloy $SnCu_4$, specific gravity 8·77, has similar properties (according to Riche). All the alloys except $SnCu_3$ (and $SnCu_4$) split up on cooling; a portion richer in copper solidifies first (this phenomenon is termed the *liquation* of an alloy), but the above two alloys do not split up on cooling. In these and many similar facts we can clearly distinguish a **chemical union between the metals** forming an alloy. The formation of the definite alloy $SnCu_3$, discovered by Riche on the basis of his researches on the densities (the density of this alloy differs considerably, according to whether it is cast or in filings; it was not determined in a molten state), was most clearly confirmed by Laurie's researches on the electro-motive force of the alloys, as this was found to be nearly the same as that of Sn or Cu before and after Cu_3Sn, and to give a marked rise for the alloy Cu_3Sn. The electrical conductivity of the alloys also exhibits a critical point for Cu_3Sn. The most fusible or eutectic (Chap. I., note 58) of the alloys rich in copper apparently has a composition about Cu_5Sn or contains 72·7 per cent. of copper. The alloys of tin and copper were known in very remote ages, before iron was used. The alloys of zinc and tin are less used, but alloys composed of zinc, tin, and copper frequently replace the more costly bronze. Concerning the alloys of lead, see note 46.

[36] An excellent proof of the fact that alloys and solutions are subject to law is given, amongst others, by the application of Raoult's method of freezing-point depression (Chap. I., note 49, and Chap. VII.) to solutions of different metals in tin. Thus, Heycock and Neville (1889) showed that the temperature of solidification of molten tin (226·4°) is always lowered by the presence of a small quantity of another metal in proportion to the concentration of the solution. The following were the reductions of the temperature of solidification of tin obtained by dissolving 11,900 parts of it in atomic proportions of different metals (for example, 65 parts of zinc); Zn 2·53°, Cu 2·47°, Ag 2·67°, Cd 2·16°, Pb 2·6°, Hg 2·3°, Sb 2·3° [rise], Al 1·34°. As this method (Chap. VII.) enables the molecular weight to be determined, the almost perfect identity of the resultant figures (except for aluminium) shows that the molecules of copper, silver, lead, and antimony contain *one atom in the molecule*, like zinc, mercury, and cadmium. They obtained the same result (1890) for Mg, Na, Ni, Au, Pd, Bi, and In. It should here be mentioned that for the same purpose (the determination of the molecular weight of metals on the basis of their mutual solution), Ramsay (1889) took advantage of the variation of the vapour pressure of mercury (Chap. VII.) containing various metals in solution, and he also found that the above-mentioned metals contain but one atom in the molecule.

a considerable quantity of water, does not act, or at all events does so only very slightly, on tin, but tin reduces hot strong sulphuric acid, when not only sulphurous anhydride but also sulphuretted hydrogen is evolved. Hydrochloric acid acts very readily on tin, with evolution of hydrogen and formation of stannous chloride, $SnCl_2$, in solution, which, with an excess of hydrochloric acid and access of air, is converted into stannic chloride or tetrachloride of tin: $SnCl_2 + 2HCl + O = SnCl_4 + H_2O$.[36a] Nitric acid diluted with a considerable quantity of water dissolves tin at the ordinary temperature, while the nitric acid itself is reduced, forming, amongst other products, ammonia and hydroxylamine. Here the tin passes into solution in the form of stannous nitrate. Stronger nitric acid (also more dilute, when heated) transforms the tin into its highest grade of oxidation, SnO_2, but the latter then appears as the so-called metastannic acid, which does not dissolve in nitric acid, and therefore the tin does not pass into solution. Feeble acids—for instance, carbonic and organic acids—do not act on tin even in the presence of oxygen, because tin does not form any powerful bases.

It is important to remark as a characteristic of tin, that it is reduced from its solutions by many metals which are more easily oxidised, as, for instance, by zinc.

In combination, tin appears in the two forms, SnX_4 and SnX_2, compounds of the intermediate type, Sn_2X_6, being also known, but these latter pass with remarkable facility in most cases into compounds of the higher and lower types, and therefore the form SnX_3[37] cannot be considered as independent.

Stannous oxide, SnO, in an anhydrous condition is obtained by boiling solutions of stannous salts with alkalies, the first action of the alkali being to precipitate a white hydrate of stannous oxide, $Sn(OH)_2,SnO$. The latter when heated parts with water as easily as the hydrate of copper oxide. In this form, stannous oxide is a black crystalline powder (specific gravity 6·7) capable of further oxidation when heated. The

---

[36a] The action of hydrochloric acid on tin forms an excellent means of reducing, wherein both the hydrogen liberated by the mixture (at the moment of separation) and the stannous chloride act as powerful reducing and deoxidising agents. Thus, for instance, by this mixture nitro-compounds are transformed into amido-compounds—that is, the elements of the group NO_2 are reduced to NH_2.

[37] Many volatile compounds of tin are known, the molecular weights of which can therefore be established from their vapour densities. Among these may be mentioned stannic chloride, $SnCl_4$, and stannic ethide, $Sn(C_2H_5)_4$ (the latter boils at about 150°). But V. Meyer found the vapour density of stannous chloride, $SnCl_2$, to be variable between its boiling-point (606°) and 1100°, owing, it would seem, to the fact that the molecule then varies from Sn_2Cl_4 to $SnCl_2$; but the vapour density proved to be less than that indicated by the first and greater than that shown by the second formula, although it approaches to the latter as the temperature rises.

hydrate is freely soluble in acids, and also in potassium and sodium hydroxides, but not in aqueous ammonia.[38] This property indicates the feeble basic properties of this lower oxide, which acts in many cases as a reducing agent.[39] Among the compounds corresponding with stannous oxide the most remarkable and the one most frequently used is stannous chloride or **chloride of tin**, $SnCl_2$, also called protochloride of tin (because it is the lowest chloride, containing half as much Cl as $SnCl_4$). It is a transparent, colourless, crystalline substance, melting at 250° and boiling at 606°. Water dissolves it, without visible change (in reality partial decomposition occurs, as we shall see presently). It is also soluble in alcohol. It is obtained by heating tin in dry hydrochloric acid gas, the hydrogen being then liberated, or by dissolving metallic tin in hot strong hydrochloric acid and then evaporating quickly. On cooling, crystals of the monoclinic system are obtained having the composition $SnCl_2,2H_2O$. An aqueous solution of this substance absorbs oxygen from the atmosphere and gives a precipitate containing stannic oxide. From this it follows that a solution of stannous chloride will act as a reducing agent; a fact frequently made use of in chemical investigations—for example, for reducing metals from their solutions—since even mercury may be reduced to a metallic state from its salts by means of stannous chloride. This reducing property is also employed in the arts, especially in the dyeing industry, where this substance in the form of a crystalline salt finds an extensive application, and is known as *tin salt* or tin crystals.

Stannic oxide, SnO_2, occurring in nature as *tinstone*, or *cassiterite*, is formed, during the oxidation or combustion of heated tin in air, as a white or yellowish powder which fuses with difficulty. It is prepared

---

[38] When rapidly boiled, an alkaline solution of stannous oxide deposits tin and forms stannic oxide, $2SnO = Sn + SnO_2$, which remains in the alkaline solution.

[39] Weber (1882), by precipitating a solution of stannous chloride with sodium sulphite (this salt, as a reducing agent, prevents the oxidation of the stannous compound) and dissolving the washed precipitate in nitric acid, obtained crystals of *stannous nitrate*, $Sn(NO_3)_2,20H_2O$, on refrigerating the solution. This crystallo-hydrate easily melts, and is deliquescent. Besides this, a more stable anhydrous basic salt, $Sn(NO_3)_2,SnO$, is easily formed. In general, stannous oxide, as a feeble base, readily forms basic salts, just as cupric and lead oxides do. For the same reason SnX_2 easily forms double salts. For instance, a potassium salt, SnK_2Cl_4,H_2O, and especially an ammonium salt, $Sn(NH_4)_2Cl_4,H_2O$, called **pink salt**, are known. Some of these salts are used in the arts, owing to their being more stable than tin salts alone. Stannous bromide and iodide, $SnBr_2$ and SnI_2, resemble the chloride in many respects.

Among other stannous salts a sulphate, $SnSO_4$, is known. It is formed as a crystalline powder when a solution of stannous oxide in sulphuric acid is evaporated under the receiver of an air-pump. It decomposes, when heated, into stannic oxide and sulphurous anhydride.

In gaseous hydrochloric acid, stannous chloride, $SnCl_2,2H_2O$, forms a liquid having the composition, $SnCl_2,HCl,3H_2O$ (sp. gr. 2·2, freezes at $-27°$).

in large quantities, being used as a white vitreous mixture for coating ordinary tiles and similar earthenware objects with a layer of easily fusible glass or enamel. Acid solutions of stannic oxide treated with alkalies, and alkaline solutions treated with acids, give a precipitate of stannic hydroxide, $Sn(OH)_4$, also known as stannic acid, which, when heated, gives up water and leaves the anhydride, SnO_2, which is insoluble in acids, clearly showing the feebleness of its basic character. When fused with alkali hydroxides (not with their carbonates or acid sulphates), an alkaline compound is obtained which is soluble in water. Stannic hydroxide, like the hydrates of silica, is a colloidal substance, and presents several different modifications, depending on the method of preparation, but having an identical composition ; the various hydroxides have also a different appearance, and act differently with reagents. For instance, a distinction is made between ordinary stannic acid and metastannic acid. **Stannic acid** is produced by precipitation by soda or ammonia from a freshly prepared solution of stannic chloride, $SnCl_4$, in water ; on drying the precipitate thus obtained, a non-crystalline mass is formed, which is freely soluble in strong hydrochloric or nitric acid, and also in potassium or sodium hydroxide. This ordinary stannic acid may be still better obtained from sodium stannate by the action of acids. **Metastannic acid** is insoluble in sulphuric or nitric acid. It is obtained in the form of a heavy white powder by treating tin with nitric acid ; hydrochloric acid does not dissolve it immediately, but changes it to such an extent that, after pouring off the acid, water extracts the stannic chloride, $SnCl_4$, already formed. Dilute alkalies not only dissolve metastannic acid, but also transform it into salts, which slowly, yet completely, dissolve *in pure water*, but are insoluble even in dilute alkali hydroxides. Dilute hydrochloric acid, especially when boiling, changes the ordinary hydrate into metastannic acid. On this depends, by the way, the formation of a white precipitate, stannic hydroxide, from solutions of stannous and stannic chlorides diluted with water. The stannic oxide first dissolved changes under the influence of hydrochloric acid into metastannic acid, which is insoluble in water in the presence of hydrochloric acid. Solutions of metastannic acid differ from solutions of ordinary stannic acid, and in the presence of alkali they change into solutions of ordinary acid, so that metastannic acid corresponds principally with the acid compounds of stannic oxide, and ordinary stannic acid with the alkaline compounds.[40] Graham

---

[40] Frémy supposes the cause of the difference to consist in polymerisation, and considers that the ordinary acid corresponds with the oxide SnO_2, and the meta-acid with the oxide Sn_5O_{10}, but it is more probable that both are polymeric, though to a different

obtained a soluble colloidal hydroxide ; it is subject to the same transformations as are in general peculiar to colloids.

Stannic oxide shows the properties of a slightly energetic and intermediate oxide (like water, silica, &c.) ; that is to say, it forms saline compounds both with bases and with acids, but both are easily decomposed, and are but slightly stable. But still the acid character is more clearly developed than the basic, as in silica, germanic oxide, and lead dioxide. This determines the character of the compounds SnX_4, corresponding to **stannic chloride**, $SnCl_4$ or tetrachloride of tin. It is obtained in an anhydrous condition by the direct action of chlorine on tin, and is then easily purified, as it is a liquid boiling at 114°. Its specific gravity is 2·28 (at 0°), and it fumes in the open air (spiritus fumans Libavii), reacting on the moisture of the air, and thus showing the properties of a chloranhydride. Water, however, does not at first decompose it, but dissolves it, and on evaporation gives the crystallohydrate, $SnCl_4,5H_2O$. If but little water is taken, crystals containing $SnCl_4,3H_2O$ are formed, which part with one-third of their water when placed under the receiver of an air-pump. A large quantity of water, however, especially on heating, gives rise to a precipitate of metastannic acid [41] and to formation of HCl.

degree. Stannic acid with sodium carbonate gives a salt of the composition Na_2SnO_3. The same salt is also obtained by fusing metastannic acid with sodium hydroxide, whilst metastannic acid gives a salt, $Na_2SnO_3,4SnO_2$ (Frémy), when treated with a dilute solution of alkali ; moreover, stannic acid is also soluble in the ordinary stannate, Na_2SnO_3 (Weber), so that both stannic acids (like both forms of silica) are capable of polymerisation, and probably only differ in its degree. In general, there is here a great resemblance to silica, and Graham obtained a solution of stannic acid by the direct dialysis of its alkaline solution. The main difference between these acids is that the meta-acid is soluble in hydrochloric acid, and gives a precipitate with sulphuric acid and stannous chloride, which do not precipitate the ordinary acid. Vignon (1889) found that more heat is evolved in dissolving stannic acid in KHO than metastannic. The polymerisation of many oxides, for example, of ZnO, CaO, Bi_2O_3, &c., must be recognised on the basis of the formation of the polyhydrates $(RO)_2H_2O$, and in general this is very likely an exceedingly common phenomenon, but it is most probably of all the case with oxide of tin.

[41] The formation of the compound $SnCl_4,3H_2O$ is accompanied by so great a contraction that these crystals, although they contain water, are heavier than the anhydrous chloride $SnCl_4$. The pentahydrated crystallo-hydrate absorbs dry hydrochloric acid, and gives a liquid of specific gravity 1·971, which at 0° yields crystals of the compound $SnCl_4,2HCl,6H_2O$ (it corresponds with the similar platinum compound), which melt at 20° into a liquid of specific gravity 1·925 (Engel).

Stannic chloride combines with ammonia ($SnCl_4 4NH_3$), hydrocyanic acid, phosphoretted hydrogen, phosphorus pentachloride ($SnCl_4,PCl_5$), nitrous anhydride and its chloranhydride ($SnCl_4,N_2O_3$ and $SnCl_4,2NOCl$), and with metallic chlorides (for example, $K_2SnCl_6,(NH_4)_2SnCl_6$, &c.). In general, a highly developed faculty for combination is observed in it.

Tin does not combine directly with iodine, but if its filings are heated in a closed tube with a solution of iodine in carbon bisulphide, it forms stannic iodide, SnI_4, in the form of red octahedra which fuse at 142° and volatilise at 295°. The fluorine compounds of

The alkali compounds of stannic oxide—that is, the compounds in which SnO_2 plays the part of an acid, corresponding with the compounds of silica—are very easily formed and are used in the arts. Their composition in most cases corresponds with the formula SnM_2O_3—that is, $SnO(MO)_2$, similar to $CO(MO)_2$, where M=K, Na. Acids, even feeble ones like carbonic acid, decompose the salts, like the corresponding compounds of alumina or silica. In order to obtain *potassium stannate*, which crystallises in rhombohedra, and has the composition $SnK_2O_3,3H_2O$, potassium hydroxide (8 parts) is fused, and metastannic acid (3 parts) gradually added. **Sodium stannate** is prepared in practice in large quantities by heating a solution of caustic soda with lead oxide and metallic tin. In this last case an alkaline solution of lead oxide is formed, and the tin acts on the solution in such a way as to reduce the lead and pass into solution. It is very remarkable that lead displaces tin when in combination with acids, whilst tin, on the contrary, displaces lead from its alkali compounds. By dissolving the mass obtained in water, and adding alcohol, sodium stannate is precipitated, and may then be dissolved in water and purified by re-crystallisation. The crystals have the composition $SnNa_2O_3,3H_2O$ if separated from hot strong solutions, and $SnNa_2O_3,10H_2O$ when crystallised at a low temperature. This salt is used as a mordant in dyeing operations. With a cold solution of sodium hydroxide, metastannic acid forms a salt of the composition $(NaHO)_2,5SnO_2,3H_2O$, from which Frémy drew his conclusions concerning the polymerism of metastannic acid. Like

tin have a special interest in the history of chemistry, because they give a series of double salts which are isomorphous with the hydrofluosilicates, SiR_2F_6, and this fact served to confirm the formula SiO_2 for silica, as the formula SnO_2 was indubitable. Although **stannic fluoride**, SnF_4, is almost unknown in the free state, its corresponding double salts are very easily formed by the action of hydrofluoric acid on alkaline solutions of stannic oxide; thus, for example, a crystalline salt of the composition SnK_2F_6,H_2O is obtained by dissolving stannic oxide in potassium hydroxide and then adding hydrofluoric acid to the solution. The barium salt, $SnBaF_6,3H_2O$, like its corresponding silicofluoride, is sparingly soluble. The more soluble salt of strontium, $SnSrF_6,2H_2O$, crystallises very well, and is therefore more important for the purposes of research; it is isomorphous with the corresponding salt of silicon (and titanium); the magnesium salt contains $6H_2O$.

Stannic sulphide, SnS_2, is formed, as a yellow precipitate, by the action of sulphuretted hydrogen on acid solutions of stannic salts; it is easily soluble in ammonium and potassium sulphides, because it has an acid character, and then forms thiostannates (see Chap. XX.). In an anhydrous state it has the form of brilliant golden yellow plates, which may be obtained by heating a mixture of finely divided tin, sulphur, and sal-ammoniac for a considerable time. It is sometimes used in this form under the name of mosaic gold, as a cheap substitute for gold-leaf in gilding wooden articles. On ignition it parts with a portion of its sulphur, and is converted into stannous sulphide, SnS. It is soluble in caustic alkalies. Hydrochloric acid does not dissolve the anhydrous crystalline compound, but the precipitated powdery sulphide is soluble in boiling strong hydrochloric acid, with the evolution of hydrogen sulphide.

other metals and many metalloids, tin gives a peroxide form of combination or **perstannic oxide**. This substance was obtained by Spring (1889) in the form of hydrate, $H_2Sn_2O_7=2(SnO_3)H_2O$, by mixing a solution of $SnCl_2$, containing an excess of HCl, with freshly prepared peroxide of barium. A cloudy liquid is then obtained, and after being subjected to dialysis this leaves a gelatinous mass which on drying is found to have the composition $Sn_2H_2O_7$. Above 100° this substance gives off oxygen and leaves SnO_2. It is evident that SnO_3 bears the same relation to SnO_2 as H_2O_2 to H_2O or ZnO_2 to ZnO, &c.

Tin occupies the same position amongst the analogues of silicon as cadmium and indium amongst the analogues of magnesium and aluminium respectively, and as in each of these cases the heavier analogues with a high atomic weight and a special combination of properties—namely, mercury and thallium—are known, so also for silicon we have **lead** (Pb=207) as the heaviest analogue, with a series of both kindred and special properties. The higher type, PbX_4—for instance, PbO_2 and $PbCl_4$—is in a chemical sense far less stable than the lower type, PbX_2, PbO, $PbCl_2$ &c. The ordinary compounds of lead correspond with the latter, and in addition to this, PbO, although not particularly energetic, is still a decided base easily forming basic salts, $PbX_2(PbO)_n$. Although the compounds PbX_4 are unstable, they offer many points of analogy with the corresponding compounds of tin, SnO_2; this is seen, for instance, from the fact that PbO_2 is a feeble acid, giving the salt PbK_2O_3, that $PbCl_4$ is a liquid like $SnCl_4$ which is not affected by sulphuric acid, and that PbF_4 gives double salts, like SnF_4 or SiF_4 (Brauner, 1894. See Chapter II., note 49a); $Pb(C_2H_5)_4$ also resembles $Sn(C_2H_5)_4$, &c. All this shows that lead is a true analogue of tin, as Hg is of cadmium.[41a]

Lead is found in nature in considerable masses, in the form of **galena**, i.e., lead sulphide, PbS.[42] The specific gravity of galena is 7·58, and its colour grey; it crystallises in the regular system, and has a fine metallic lustre. Both the native and artificial sulphides are insoluble in acids (hydrogen sulphide gives a black precipitate with the salts PbX_2).[42a] When heated, lead melts, and in the open air is either

---

[41a] Although the analogy between Sn and Pb has long been generally recognised from the resemblance between the two metals, from a chemical point of view it has only been demonstrated by means of the periodic·law.

[42] Mixed ores of copper compounds, together with PbS and ZnS, are frequently found in the most ancient primary rocks. As the separation of the metals themselves is difficult, the ores are separated by a method of selection or mechanical sorting. Such mixed ores occur in Russia, in many parts of the Caucasus, and in the Donetz district (at Nagolchik).

[42a] Lead sulphide in the presence of zinc and hydrochloric acid is completely reduced to metallic lead, all the sulphur being given off as hydrogen sulphide.

totally or partially transformed into white lead sulphate, $PbSO_4$, as it also is by many oxidising agents (hydrogen peroxide, potassium nitrate). Lead sulphate is also insoluble in water,[43] and lead is but rarely met with in this form in nature. The chromates, vanadates, phosphates, and similar salts of lead are also somewhat rare. The carbonate, $PbCO_3$, is sometimes found in large masses, especially in the Altai region. Lead sulphide is often worked for extracting the silver which it contains; and as the lead itself also finds manifold industrial applications, this work is carried out on an exceedingly large scale. Many methods are employed. Sometimes the lead sulphide is decomposed by heating it with cast iron. The iron takes up the sulphur from the lead and forms readily fusible iron sulphide, which does not mix with the heavier reduced lead. But another process is more frequently used: the lead ore (it must be clean, that is, free from earthy matter, which may easily be removed by washing) is heated in a reverberatory furnace to a moderate temperature with a free access of air. During this operation part of the lead sulphide oxidises and forms lead sulphate, $PbSO_4$, and lead oxide. When the oxidation of part of the lead has been attained, it is necessary to shut off the air supply and raise the temperature, the oxidised compounds of the lead then entering into reaction with the remaining lead sulphide, with formation of sulphurous anhydride and metallic lead. At first, from $PbS+O_3$, $PbO+SO_2$ are formed, and also from $PbS+O_4$ lead sulphate $PbSO_4$; then PbO and $PbSO_4$ react with the remaining PbS, according to the equations: $2PbO+PbS=3Pb+SO_2$ and $PbSO_4+PbS=2Pb+2SO_2$.[44]

The appearance of lead is well known; its specific gravity is 11·3; the bluish colour and metallic lustre of freshly cut lead quickly

---

[43] Lead sulphate, $PbSO_4$, occurs in nature (*anglesite*) in transparent brilliant crystals which are isomorphous with barium sulphate, and have a specific gravity of 6·3. The same salt is formed on mixing sulphuric acid or its soluble salts with solutions of lead salts, as a heavy white precipitate, which is insoluble in water and acids, but dissolves in a solution of ammonium tartrate in the presence of an excess of ammonia. This test serves to distinguish this salt from the similar ones of strontium and barium.

[44] According to J. B. Hannay (1894) the last-named decomposition ($PbS+PbSO_4=2Pb+2SO_2$) is really much more complicated, and in fact a portion of the PbS is dissolved in the Pb, forming a slag containing PbO, PbS, and $PbSO_4$, whilst a portion of the lead *volatilises* with the SO_2 in the form of a compound PbS_2O_2, which is also formed in other cases, but has not yet been thoroughly studied.

Besides these methods for extracting lead from PbS in its ores, roasting (the removal of the S in the form of SO_2) and smelting with charcoal with a blast in the same manner as in the manufacture of pig iron (Chap. XXII.) are also employed.

As lead is easily reduced from its ores, and the ore itself has a metallic appearance, it is not surprising that it was known to the ancients, and that its properties were familiar to the alchemists, who called it 'Saturn.' Hence metallic lead, reduced from its salts in solution by zinc, having the appearance of a tree-like mass of crystals, is called 'arbor Saturni,' &c.

disappear when it is exposed to the air, because it becomes coated with a layer—although a very thin one—of oxide and salts formed by the moisture and acids in the atmosphere. It melts at 320° and crystallises in octahedra on cooling. Its softness is apparent from the flexibility of lead pipes and sheets, and also from the fact that it may be cut with a knife, and also that it leaves a grey streak when rubbed on paper. On account of its being so soft, lead naturally cannot be applied in many cases where most metals may be used; but, on the other hand, it is a metal which is not easily changed by chemical reagents, and as it is capable of being soldered and drawn into sheets, &c., lead is most valuable for many other technical uses. Lead pipes are used for conveying water[45] and many other liquids, and sheet lead is used for lining all kinds of vessels containing liquids (acids, for instance) which act on other metals. This particularly refers to sulphuric and hydrochloric acids, because at ordinary temperatures these do not act on lead, and if they form lead sulphate, $PbSO_4$, and chloride, $PbCl_2$, these salts, being insoluble in water and in acids, cover the lead and protect it from further corrosion.[46] All soluble preparations of lead are poisonous. At a white heat lead may be partially distilled; the vapours oxidise and burn. Lead may also be easily oxidised at low temperatures. Lead only decomposes water at a white heat, and does not liberate hydrogen from acids, with the exception only of very strong hydrochloric acid, and this only when boiling. Sulphuric acid diluted with water does not act on it, or only acts very feebly at the surface; but strong sulphuric acid, when heated, is decomposed by it, with the evolution of sulphurous anhydride. The best solvent for lead is nitric acid, which transforms it into a soluble salt, $Pb(NO_3)_2$.

---

[45] Freshly laid new lead pipes contaminate the water with a certain amount of lead salts, arising from the presence of oxygen, carbonic acid, &c., in the water. But the lead pipes under the action of running water soon become coated with a film of salts—lead sulphate, carbonate, chloride, &c.—which are insoluble in water, and the pipes then become harmless.

[46] Lead is used in the arts, and, owing to its considerable density, it is cast, mixed with small quantities of other metals, into shot. A considerable amount is employed (together with mercury) in extracting gold and silver from poor ores, and in the manufacture of chemical reagents, and especially of lead chromate. *Lead chromate*, $PbCrO_4$, is distinguished for its brilliant yellow colour, owing to which it is employed in considerable quantities as a dye, mainly for dyeing cotton tissues yellow. It is formed on the tissue itself, by causing a soluble salt of lead to react on potassium chromate. Lead chromate is met with in nature as 'red lead ore.' It is insoluble in water and acetic acid, but dissolves in aqueous potash. So-called pewter vessels often consist of an alloy of 5 parts of tin and 1 of lead, and solder is composed of 1 to 2 parts of tin with $\frac{1}{2}$ part of lead. Amongst the alloys of lead and tin, the alloy $PbSn_3$ stands out from the rest (according to Kupfer and Rydberg), since the temperature remains constant at 187° when an alloy of this composition solidifies. All the other alloys have a higher melting-point. It is evident that this is the eutectic point (Chap. I., note 58).

Although acids thus have directly but little effect on lead, and this is one of its most important practical properties, **yet when air has free access, lead** (like copper) **very easily reacts with many acids,** even with those which are comparatively feeble. The action of acetic acid on lead is particularly striking and is often applied in practice. If lead is plunged into acetic acid it does not change at all and does not pass into solution, but if part of the lead is immersed in the acid, while the other part remains in contact with the air, or if lead is merely covered with a thin layer of acetic acid in such a way that the air is practically in contact with the metal, then it unites with the oxygen of the air to form oxide, which combines with the acetic acid and forms lead acetate, soluble in water. Not only is the normal lead acetate formed, but also basic salts.[47]

When oxidising in the presence of air,[48] when heated or in the presence of an acid at the ordinary temperature, lead forms compounds of the type PbX_2. **Lead oxide,** PbO, is known industrially as **litharge** or silberglätte (this name is due to the fact that silver is extracted from the lead ores of this kind) and massicot. If the lead is oxidised in air at a high temperature, the oxide which is formed fuses, and on cooling is easily obtained in fused masses which split up into scales of a yellowish-

---

[47] The normal lead acetate, known in trade as **sugar of lead,** owing to its having a sweetish taste, has the formula $Pb(C_2H_3O_2)_2,3H_2O$. This salt only crystallises from acid solutions. It is capable of dissolving a further quantity of lead oxide or of metallic lead in the presence of air. A basic salt of the composition $Pb(C_2H_3O_2)_2,PbH_2O_2$ is then formed which is soluble in water and alcohol. As in this salt the number of atoms is even and the same as in the hydrate of acetic acid, $C_2H_4O_2,H_2O = C_2H_3(OH)_3$, it may be represented as this hydrate in which two of hydrogen are replaced by lead—that is, as $C_2H_3(OH)(O_2Pb)$. This basic salt is used in medicine for bandaging wounds (lead salve), &c., and also in the manufacture of white lead. Other basic acetates of lead, containing a still greater amount of lead oxide, are known. According to the above representation of the composition of the preceding lead acetate, a basic salt of the composition $(C_2H_3)_2(O_2Pb)_3$ would also be possible, but what appear to be still more basic salts are known. As the character of a salt also depends on the property of the base from which it is formed, it would seem that lead forms a hydroxide of the composition HOPbOH, containing two water residues, one or both of which may be replaced by the acid residues. If both water residues are replaced, a normal salt, XPbX, is obtained, whilst if only one is replaced a basic salt, XPbOH, is formed. But lead gives not only this normal hydroxide, but also polyhydroxides, $Pb(OH),nPbO$, and if we may imagine that in these polyhydroxides there is a substitution of both the water residues by acid residues, then the power of lead to form basic salts is explained by the properties of the base which enters into their composition.

[48] Few compounds are known of the lower type PbX, and still fewer of the intermediate type PbX_3. To the first type belongs the so-called lead suboxide, Pb_2O, obtained by the ignition of lead oxalate, C_2PbO_4, without access of air. It is a black powder, which easily breaks up under the action of acids, and even by the simple action of heat, into metallic lead and lead oxide. This is the character of all suboxides. It is difficult to regard them as independent salt-forming oxides, because they have not the colour of salts. Such is red lead (see further on).

grey colour, having a specific gravity of 9·3; in this form it bears the name of litharge. Litharge is principlly used for making lead salts, for the extraction of metallic lead, and also for the preparation of drying oils—for instance, from linseed oil.[49] When oxidised carefully and slightly heated, lead forms a powdery (not fused) oxide known under the name of **massicot.** It is best prepared in the laboratory by heating lead nitrate, or lead hydroxide. It has a yellow colour, and when moistened with water does not attract the carbonic acid of the air so easily as litharge does, owing to the superficial formation of dioxide on which acids do not act. In any case lead oxide is comparatively easily soluble in nitric and acetic acids. It is but slightly soluble in water, but communicates an alkaline reaction to it, since it forms the hydroxide. This **hydroxide** is obtained in the shape of a white precipitate by the action of a small quantity of an alkali hydroxide on a solution of a lead salt. An excess of alkali dissolves the hydroxide separated, which fact demonstrates the comparatively indistinct basic properties of lead oxide. The normal lead hydroxide, which should have the composition $Pb(OH)_2$, is unknown in a separate state, but it is known in polymeric combination with lead oxide as $Pb(OH)_2,2PbO$ or $Pb_3O_2(OH)_2$. The latter is obtained in the form of brilliant white octahedral crystals when basic lead acetate is mixed with ammonia and gently heated. It absorbs the carbonic anhydride of the air. When an alkaline solution of the hydroxide is boiled, it deposits lead oxide in the form of a crystalline powder.

Lead oxide forms but few soluble salts—for instance, the nitrate and the acetate. The majority of its salts (sulphate, $PbSO_4$; carbonate, $PbCO_3$; iodide, PbI_2, &c.) are insoluble in water. These salts are colourless or pale yellow if the acid is colourless. In lead oxide **the faculty of forming basic salts,** $PbX_2,nPbO$ or $PbX_2,nPbH_2O_2$, is strongly developed. A similar property was observed in magnesium and also in the salts of mercury, but lead oxide forms basic salts with still greater facility, although double salts are in this case more rarely formed.[50]

---

[49] In the boiling of drying oils (linseed, poppy seed, &c.), the lead oxide passes partially into solution, forming a saponified compound capable of attracting oxygen and solidifying to a tarlike mass, which forms the oil paint. Perhaps, however, glycerine has some action in the process. Ossovetsky, by saturating drying oil with the salts of certain metals, obtained oil colours of great durability.

A mixture of very finely divided litharge with glycerine (50 grams of litharge to 5 c.c. of anhydrous glycerine) forms a very quick (two minutes) setting cement, which is insoluble in water and oils, and is very useful in setting up chemical apparatus.

[50] It is very instructive to observe that lead easily forms not only basic salts, but also salts containing several acid groups. Thus, for example, lead carbonate forms compounds with lead chloride and sulphate. The first compound known as **corneous lead**

Amongst the soluble lead salts, that best known and most often applied in practical chemistry is **lead nitrate,** $Pb(NO_3)_2$, obtained directly by dissolving lead or its oxide in nitric acid. It crystallises in octahedra, and has a specific gravity of 4·5. When a solution of this salt is boiled with litharge, the basic salt, having a composition $Pb(OH)(NO_3)$, is formed in crystalline needles, sparingly soluble in cold water but easily dissolved in hot water, and therefore much resembling lead chloride. When the nitrate is heated, either lead oxide is obtained or else the oxide in combination with peroxide. **Lead chloride,** $PbCl_2$, is precipitated from the soluble salts of lead when strong solutions are treated with hydrochloric acid or a metallic chloride. It is soluble in considerable quantities in hot water, and therefore, if the solutions be dilute or hot, the precipitation of lead chloride does not occur, and if the solution be cooled, the salt separates in brilliant prismatic crystals. It easily fuses when heated (like silver chloride), but is insoluble in ammonia. This salt is sometimes met with in nature, and when heated in air is capable of exchanging half its chlorine for oxygen, forming the basic salt or lead oxychloride, $PbCl_2,PbO$, which may also be obtained by fusing $PbCl_2$ and PbO together. The reaction of lead chloride with water vapour leads to the same conclusion, showing the feeble basic character of oxide of lead, $2PbCl_2+H_2O=PbCl_2,PbO+2HCl$. When ammonia is added to an aqueous solution of lead chloride a white precipitate is formed, which parts with water on being heated, and has the composition $Pb(OH)Cl,PbO$. This compound is also formed by the action of metallic chlorides on other soluble basic salts of lead.[51]

---

or *phosgenite*, has the composition $PbCO_3,PbCl_2$; it occurs in nature in bright cubic crystals, and is prepared artificially by simply boiling lead chloride with lead carbonate. A similar compound of normal salts, $PbSO_4,PbCO_3$, occurs in nature as **lanarkite** in monoclinic crystals. **Leadhillite** has the composition $PbSO_4,3PbCO_3$, and also occurs in yellowish, monoclinic, tabular crystals. In describing silica we carefully developed the conception of polymerisation, which it is *also indispensable to recognise in the composition of many other oxides.* Thus it may be supposed that PbO and PbO_2 are polymerised compounds similar to SiO_2—i.e., that the compositition of lead peroxide will be Pb_nO_{2n} and that of the oxide Pb_nO_n. This consideration respecting the complexity of lead oxide could have no real significance, and could not be accepted, were it not for the existence of the above-mentioned basic and mixed salts. The oxide apparently corresponds with the composition Pb_nX_{2n}, and since, according to this representation, the number of X's in the salts of lead is considerable, it is obvious that they may be diverse. When a part of these X's is replaced by the water residue (OH) or by oxygen, $X_2=O$, and the other parts by an acid residue X, basic salts are obtained; but if a part of the X's is replaced by acid residues of one kind, and the other part by acid residues of another kind, then those mixed salts about which we are now speaking are formed. The theory of the polymerisation of oxides introduced by me in the first edition of this work (1869) is now beginning to be generally accepted, and has been applied by many in investigating the hydrates and basic salts of different metals.

[51] A similar basic salt having a white colour, and therefore used as a substitute for

Lead carbonate, or **white lead**, is the most extensively used basic lead salt. It has the valuable faculty of 'covering,' to a greater extent than appertains to other substances. This faculty consists in the fact that a small quantity of white lead mixed with oil spreads uniformly, and if such a mixture is spread over a surface (for instance, of wood or metal), light does not penetrate through, so that the grain of the wood remains invisible.[52] White lead, or **basic lead carbonate**, after being dried at 120°, has the composition $Pb(OH)_2,2PbCO_3$.[53] It may be obtained by adding a solution of sodium carbonate to a solution of one of the basic salts of lead—for instance, the basic acetate—and likewise by treating this latter with carbonic acid. For this purpose the solution of basic acetate is poured into the vessel *f*; it is prepared in the vat A, containing litharge, into which the pump P delivers the solution of the acetate, which remains after the action of carbonic anhydride on the basic salt. In A a basic salt is formed having a composition approaching to $Pb_4(OH)_6(C_2H_3O_2)_2$; carbonic anhydride, $2CO_2$, is passed through this solution and precipitates white lead, $Pb_2(OH)_2(CO_3)_2$, while normal lead acetate, $Pb(C_2H_3O_2)_2$, remains in the solution, and is pumped back into the vat A containing lead

---

white lead, is also obtained by mixing a solution of basic lead acetate with a solution of lead chloride. Its formation is expressed by the equation: $2PbX(OH),PbO+PbCl_2 = 2Pb(OH)Cl,PbO+PbX_2$. Similar basic compounds of lead are met with in nature —for instance, *mendipite*, $PbCl,2PbO$, which appears in brilliant yellowish-white masses. The ignition of red lead with sal-ammoniac results in similar polybasic compounds of lead chloride, forming *Cassel's* or *mineral yellow* of the composition $PbCl_2,nPbO$. **Lead iodide**, PbI_2, is still less soluble than the chloride, and is therefore obtained by mixing potassium iodide with a solution of a lead salt. It separates as a yellow powder, which may be dissolved in boiling water, and on cooling separates in very brilliant crystalline scales of a golden-yellow colour. The salts $PbBr_2$, PbF_2, $Pb(CN)_2$ $Pb_2Fe(CN)_6$ are also insoluble in water, and form white precipitates

[52] It is remarkable that a peculiar kind of attraction exists between boiled linseed oil and white lead, as is seen from the following experiments. White lead is triturated in water. Although it is heavier than water, it remains in suspension in it for some time and is thoroughly moistened by it, so that the trituration may be made perfect; boiled linseed oil is then added, and shaken up with it. A mixture of the oil and white lead is then found to settle at the bottom of the vessel. Although the oil is lighter than the water it does not float on the top, but is retained by the white lead and sinks with it under the water. There is not, however, any more perfect combination nor even any solution. If the resultant mass be then treated with ether or any other liquid capable of dissolving the oil, the latter passes into solution and leaves the white lead unaltered.

[53] White lead may be regarded as a salt corresponding with the normal hydrate of carbonic acid, $C(OH)_4$, in which three-quarters of the hydrogen is replaced by lead. A salt is also known in which all the hydrogen of this hydrate of carbonic acid is replaced by lead—namely, the salt of the composition CO_4Pb_2. This salt is obtained as a white crystalline substance by the action of water and carbonic acid on lead. The normal salt, $PbCO_3$, occurs in nature under the name of white lead ore (sp. gr. 6·47), in crystals isomorphous with aragonite, and is formed as a heavy white precipitate by the double decomposition of lead nitrate with sodium carbonate.

oxide, where the normal salt is again (on being agitated) converted into the basic salt. This is run into the vessel E, and thence into *f*. Into the latter, carbonic anhydride is delivered from the generator D, and forms a precipitate of white lead.[53a]

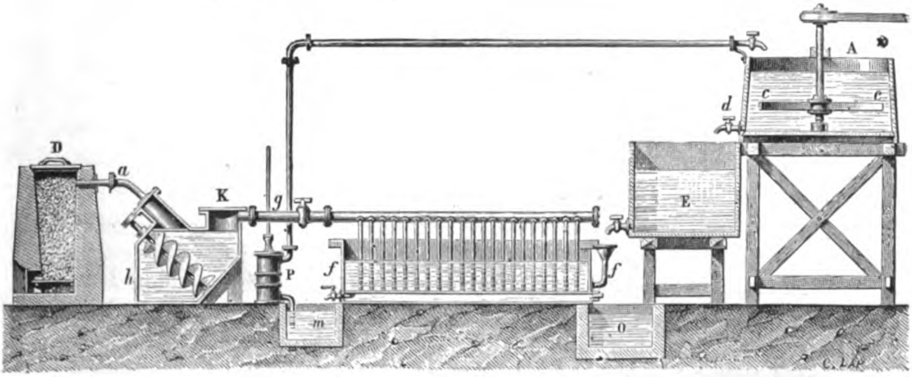


FIG. 93.—Apparatus for the manufacture of white lead.

In order to mark the transition from lead oxide, PbO, into lead dioxide PbO_2 (plumbic anhydride), it is necessary to direct our attention to the intermediate oxide, or **red lead**, Pb_3O_4.[54] In the arts it is used in considerable quantities, because it forms a very durable yellowish-red paint used for colouring the resins (shellac, colophony, &c.) composing sealing-wax. It also forms a very good cheap oil paint, used especially for painting metals, more particularly because drying oils—for instance, hempseed and linseed oils—quickly dry with red lead and with lead salts. Red lead is prepared by slightly heating

---

[53a] One of the many methods by which white lead is prepared consists in mixing massicot with acetic acid or sugar of lead, and leaving the mixture exposed to air (and re-mixing from time to time) containing carbonic acid, which is absorbed from the surface by the basic salt formed. After repeated mixings (with the addition of water), the entire mass is converted into white lead, which is thus obtained very finely divided.

[54] If lead hydroxide is dissolved in potash and sodium hypochlorite is added to the solution, the oxygen of the latter acts on the dissolved lead oxide, and partially converts it into dioxide, so that the so-called **lead sesquioxide** is obtained; its empirical formula is Pb_2O_3. Probably it is nothing but lead plumbate—i.e., hydroxide of dioxide of lead, $PbO(OH)_2$, in which two atoms of hydrogen are replaced by lead, $PbO(O_2Pb)$. The brown compound precipitated by the action of dilute acids—for example, nitric—splits up, even at the ordinary temperature, into insoluble lead dioxide and a solution of a lead salt. This compound evolves oxygen when it is heated. It dissolves in hydrochloric acid, forming a yellow liquid, which probably contains compounds of the composition $PbCl_2$ and $PbCl_4$; but even at the ordinary temperature the latter soon loses the excess of chlorine, and then only lead chloride, $PbCl_2$, remains. In order to see the relation between red lead, Pb_3O_4, and lead sesquioxide, it must be observed that they only differ by an extra quantity of lead oxide—that is, red lead is a basic salt of the preceding compound.

massicot in air, for which purpose two-storied stoves are used. In the lower story the lead is turned into massicot, and in the higher one, having the lower temperature (about 300°), the massicot is transformed into red lead. Frémy and others showed the instability of red lead prepared by various methods, and its decomposition by acids, with formation of lead dioxide, which is insoluble in acids, and a solution of the salts of lead oxide. The artificial production (synthesis) of red lead by double decomposition was most important. For this purpose Frémy mixed an alkaline solution of **potassium plumbate**, K_2PbO_3 (prepared by dissolving the dioxide in fused potash),[54a] with an alkaline solution of lead oxide. In this way a yellow precipitate of minium hydrate is formed, which, when slightly heated, loses water and turns into bright red anhydrous minium, Pb_3O_4.

Minium is the first and most ordinary means of producing **lead dioxide**, or plumbic anhydride, PbO_2,[55] because when red lead is treated with dilute nitric acid it gives up lead oxide, and leaves PbO_2 on which dilute nitric acid does not act. The composition of minium is Pb_3O_4, and therefore the action of nitric acid on it is expressed by the equation : $Pb_3O_4+4HNO_3=PbO_2+2Pb(NO_3)_2+2H_2O$. The dioxide may also be obtained by treating lead hydroxide suspended in

---

[54a] Frémy obtained **potassium plumbate** in the following manner. Pure lead dioxide is placed in a silver crucible, and a strong solution of pure caustic potash is poured over it. The mixture is heated and small quantities are removed from time to time for testing, which consists in dissolving in a small quantity of water and decomposing the resultant solution with nitric acid. There is a certain moment during the heating when a considerable amount of insoluble lead dioxide is precipitated on the addition of the nitric acid ; the solution then contains the salt in question, and the heating must be stopped, and a small amount of water added to dissolve the potassium plumbate formed. On cooling, the salt separates in somewhat large crystals, which have the same composition as the stannate—that is, $PbO(KO)_2,3H_2O$.

[55] Lead dioxide is often called **lead peroxide** ; but this name leads to error, because PbO_2 does not show the properties of true peroxides, like those of hydrogen or barium, but is endowed with acid properties—that is, it is able to form true salts with bases, which is not the case with true peroxides. Lead dioxide is a normal salt-forming compound of lead, as Bi_2O_5 is for bismuth, CeO_2 for cerium, and TeO_3 for tellurium, &c. They all evolve chlorine when treated with hydrochloric acid, whilst true peroxides form hydrogen peroxide. The true lead peroxide, if it were obtained, would probably have the composition Pb_2O_5, or, in combination with peroxide of hydrogen, $H_2Pb_2O_7=H_2O_2+Pb_2O_5$, judging from the peroxides corresponding with sulphuric, chromic, and other acids, which we shall afterwards consider.

As a proof of the fact that the form PbO_2, or PbX_4, is the highest normal form of any combination of lead, it is most important to remark that it might be expected that the action of lead chloride, $PbCl_2$, on zinc-ethyl, $ZnEt_2$, would result in the formation of zinc chloride, $ZnCl_2$, and lead-ethyl, $PbEt_2$, but that in reality the reaction proceeds otherwise. Half of the lead is set free, and lead tetrethyl, $PbEt_4$, is formed as a colourless liquid, boiling at about 200° (Butleroff, Frankland, Buckton, Cahours, and others). The type PbX_4 is not only expressed in $PbEt_4$ and PbO_2, but also in PbF_4, obtained by Brauner (Chap. XI., note 49a).

water with a stream of chlorine. Under these conditions the chlorine takes up the hydrogen from the water, and the oxygen passes over to the lead oxide.[56] When a strong solution of lead nitrate is decomposed by the electric current, the appearance of crystalline lead dioxide is also observed upon the positive pole; it is also found in nature in the form of a black crystalline substance having a specific gravity of 9·4. When artificially produced it is a fine dark powder, resisting the action of acids, but nevertheless when treated with strong sulphuric acid it evolves oxygen and forms lead sulphate, and with hydrochloric acid it evolves chlorine. The oxidising property of lead dioxide depends of course on the facility of its transition into the more stable lead oxide, which is easily understood from the whole history of lead compounds. In the presence of alkalies it transforms chromium oxide into chromic acid, lead chromate, $PbCrO_4$, being formed and remaining in solution, on account of its being soluble in caustic alkalies. The oxidising action of lead dioxide on sulphurous anhydride is most striking, as it immediately absorbs it, with formation of lead sulphate. This is accompanied by a change of colour and development of heat, $PbO_2+SO_2=PbSO_4$. When triturated with sulphur the mixture explodes, the sulphur burning at the expense of the oxygen of the lead dioxide. **Tetrachloride of lead**, $PbCl_4$, belongs to the same class of lead compounds as PbO_2. This chloride is formed by the action of strong hydrochloric acid upon PbO_2, or, in the cold, by passing a stream of chlorine through water containing $PbCl_2$ in suspension. The resultant yellow solution gives off chlorine when heated. With a solution of sal-ammoniac (Nikolukine, 1885) it gives a precipitate of a double salt, $(NH_4)_2PbCl_6$ (very slightly soluble in a solution of sal-ammoniac), which when treated with strong sulphuric acid (Friedrich, 1890) gives $PbCl_4$ as a yellow liquid of sp. gr. 3·18, which solidifies at $-18°$, and when heated gives $PbCl_2+Cl_2$. It is not acted upon by H_2SO_4, like $SnCl_4$. Tetrafluoride of lead (Brauner) belongs to the same class of compounds; it easily forms double salts and decomposes with evolution of fluorine (Chap. II., note 49a).[56a]

[56] According to Carnelley and Walker, the hydrate $(PbO_2)_3,H_2O$ is then formed; it loses water at 230°. The anhydrous dioxide remains unchanged up to 280°, and is then converted into the sesquioxide, Pb_2O_3, which again loses oxygen at about 400°, and forms red lead, Pb_3O_4. Red lead also loses oxygen at about 550°, forming lead oxide, PbO, which fuses without change at about 600°, and remains constant as far as the limit of the observations made (about 800°).

The best method for preparing pure lead dioxide consists in mixing a hot solution of lead chloride with a solution of bleaching powder (Fehrman). Under the action of a galvanic current, lead salts give not only PbO_2, but also its compounds; for instance, $Pb(SO_4)_2$, which may be regarded as a salt of persulphuric acid and PbO.

[56a] The plumbates of Ca and other similar metals, mentioned in Chap. III., note 7, also belong to the form PbX_4.

In the second and third groups it was observed that the elements were more basic in the even than in the uneven series. It is sufficient to remember calcium, strontium, and barium in the even, and magnesium, zinc, and cadmium in the uneven series. In addition to this, in the even series, as the atomic weight increases, in the same type of oxidation the basic properties increase (the acid properties decrease); for example, in the second group, calcium, strontium, barium. The same also appears in the fourth and all the following groups. In the even series of the fourth group, titanium, zirconium, cerium, and thorium are found. All their highest oxides, RO_2, even the lightest—titanic oxide, TiO_2—have more highly developed basic properties than silica, SiO_2, and in addition to this the basic properties are more distinctly seen in zirconium dioxide, ZrO_2, than in titanic oxide, TiO_2, although the acid property of combining with bases still remains. In the heaviest oxides, cerium dioxide, CeO_2, and thorium dioxide, ThO_2, no acid properties are observed, these being both purely basic oxides. This higher oxide of cerium has already been described in the preceding chapter, and as titanium and zirconium are rather rare in nature, have but little practical application, and do not present any new forms of combination, it is inadvisable to dwell on them in this treatise.

Titanium is found in nature in the form of its anhydride or oxide, TiO_2, mixed with silicon in many silicious minerals (even in clay and bauxite), but the oxide is also found separately in the form of semi-metallic **rutile** (sp. gr. 4·2). Another titanic mineral is found as a mixture in other ores, known as **titanic iron ore** (in the Thuensky mountains of the southern Ural; it is known as *thuenite*), $FeTiO_3$. This is a salt of ferrous oxide and titanic anhydride. It crystallises in the rhombohedral system, has a metallic lustre, a grey colour, and the sp. gr. 4·5. The third mineral in which titanium is found in considerable quantities in nature is *sphene* or *titanite*, $CaTiSiO_5 = CaO,SiO_2,TiO_2$, sp. gr. 3·5, colour yellow, green, or the like, crystallises in tablets. The fourth, but rare, titanic mineral is *peroffskite*, calcium titanate, $CaTiO_3$; it forms blackish-grey or brown cubic crystals, sp. gr. 4·02, and occurs in the Ural and other localities. It may be prepared artificially by fusing sphene in an atmosphere of water vapour and carbonic anhydride. At the end of the last century Klaproth showed the distinction between titanic compounds and all others then known.[57]

---

[57] The compounds of titanium are generally obtained from rutile; the finely ground ore is fused with a considerable amount of acid potassium sulphate, until the titanic anhydride, as a feeble base, passes into solution. After cooling, the resultant mass is ground up, dissolved in cold water, and treated with ammonium hydrosulphide; a black precipitate then separates out from the solution. This precipitate contains TiO_2 (as

The comparatively rare element **zirconium**, Zr=90, is very similar to titanium, and has a more basic character. It is rarer in nature

---

hydrate) and various metallic sulphides—for example, iron sulphide. It is first washed with water and then with a solution of sulphurous anhydride until it becomes colourless. This is due to the iron sulphide, which is contained in the precipitate, and renders it black, being converted into dithionate by the action of the sulphurous acid. The titanic acid left behind is nearly pure. The considerable volatility of titanium chloride may also be taken advantage of in preparing the compounds of titanium from rutile. It is formed by strongly heating a mixture of rutile and charcoal in dry chlorine; the distillate then contains **titanium chloride**, $TiCl_4$. It may be easily purified, owing to its having a constant boiling-point of 136°. Its specific gravity is 1·76; it is a colourless liquid, which fumes in the air, and is perfectly soluble in water if it is not heated. When hot water acts on titanic chloride, a large proportion of titanic acid separates out from the solution and passes into metatitanic acid. A similar decomposition of acid solutions of titanic acid is accomplished whenever they are heated, and especially in the presence of sulphuric acid, just as with metastannic acid, which titanic acid resembles in many respects. On igniting the titanic acid a colourless powder of the anhydride, TiO_2, is obtained. In this form it is no longer soluble in acids or alkalies, and only fuses in the oxy-hydrogen flame; but, like silica, it dissolves when fused with alkalies or their carbonates; as already mentioned, it dissolves when fused with a considerable excess of acid potassium sulphate—that is, it then reacts as a feeble base. This shows the basic character of titanic anhydride; it has at once, although feebly developed, both basic and acid properties. The fused mass, obtained from titanic anhydride and alkali when treated with water, parts with its alkali, and a residue is obtained of a sparingly soluble poly-titanate, $K_2TiO_3,nTiO_2$. The hydrate, which is precipitated by ammonia from the solutions obtained by the fusion of TiO_2 with acid potassium sulphate, when dried forms an amorphous mass of the composition $Ti(OH)_4$. But it loses water over sulphuric acid, gradually passing into a hydrate of the composition $TiO(OH)_2$, and when heated it parts with a still larger proportion of water; at 100° the hydrate $Ti_2O_3(OH)_2$ is obtained, and at 300° the anhydride itself. The higher hydrate, $Ti(OH)_4$, is soluble in dilute acid, and the solution may be diluted with water; but on boiling the sulphuric acid solution (though not the solution in hydrochloric acid), all the titanic acid separates in a modified form, which is, however, not only soluble in dilute acids, but even in strong sulphuric acid. This hydrate has the composition $Ti_2O_3(OH)_2$, but shows different properties from those of the hydrate of the same composition described above, so that this modified hydrate is called **metatitanic acid**. It is most important to note the property of the ordinary gelatinous hydrate (that precipitated from acid solutions by ammonia) of dissolving in acids, the more so since silica does not show this property. In this property a transition apparently appears between the cases of common solution (based on a capacity for unstable combination) and the case of the formation of a hydrosol (the solubility of germanium oxide, GeO_2, perhaps presents another such instance). When heated in hydrogen, TiO_2 gives a sesquioxide, Ti_2O_3, which forms alums, like Al_2O_3. If titanium chloride be added drop by drop to a dilute solution of alcohol and hydrogen peroxide, and then ammonia be added to the resultant solution, a yellow precipitate of *titanium trioxide*, TiO_3,H_2O, separates out, as has been shown by Piccini, Weller, Classen, and Levy. This substance apparently belongs to the category of true peroxides.

Titanium chloride absorbs ammonia and forms a compound, $TiCl_4,4NH_3$, as a reddish-brown powder which attracts moisture from the air and when ignited forms **titanium nitride**, Ti_3N_4. Phosphoretted hydrogen, hydrocyanic acid, and many similar compounds are also absorbed by titanium chloride, with the evolution of a considerable amount of heat. Thus, for example, a yellow crystalline powder of the composition $TiCl_4,2HCN$ is obtained by passing dry hydrocyanic acid vapour into cold titanium chloride. Metallic titanium, obtained as a grey powder by reducing potassium titanofluoride, K_2TiF_6 (sp. gr. 3·55, K. Hofman, 1893), with iron in a charcoal crucible, combines directly with nitrogen at a red heat. If titanic anhydride be ignited in a stream of ammonia, all the than titanium, and is found principally in a mineral called *zircon*, $ZrSiO_4 = ZrO_2,SiO_2$, crystallising in square prisms of sp. gr. 4·5. It has considerable hardness and a characteristic brownish-yellow colour, and is occasionally found in the form of transparent crystals, as a precious stone called hyacinth.[58] Metallic **zirconium** was obtained, by Berzelius

oxygen of the titanic oxide is disengaged, and the compound TiN_2 is formed as a dark violet substance having a copper-red lustre. A compound Ti_5N_6 is also known; it is obtained by igniting the compound Ti_3N_4 in a stream of hydrogen, and is of a golden-yellow colour with a metallic lustre. To this order of compounds belongs also the well-known and chemically historical compound known as **titanium nitrocyanide**; its composition is Ti_5CN_4. This substance appears as infusible, sometimes well formed, cubic crystals of sp. gr. 4·3, and having a red copper colour and metallic lustre; it is found in blast furnace slag. It is insoluble in acids, but is acted on by chlorine at a red heat, forming titanium chloride. It was at first regarded as metallic titanium; it is formed in the blast furnace at the expense of those cyanogen compounds (potassium cyanide and others) which are always present, and of the titanium compounds which accompany the ores of iron. Wöhler, who investigated this compound, obtained it artificially by heating a mixture of titanic oxide with a small quantity of charcoal, in a stream of nitrogen, and thus proved the direct power for combination between nitrogen and titanium. When fused with caustic potash, all the nitrogen compounds of titanium evolve ammonia and form potassium titanate. Like metals, they are able to reduce many oxides—for example, those of copper—at a red heat. Among the alloys of titanium, the crystalline compound Al_4Ti is remarkable. It is obtained by directly dissolving titanium in fused aluminium; its specific gravity is 3·11. The crystals are very stable, and are only soluble in aqua regia and alkalies.

[58] The formula ZrO was first given to the basic oxide of zirconium, taking $Zr = 45$; the present atomic weight, however, is $Zr = 90·6$, so that the formula of the oxide is now recognised as being ZrO_2. The reasons for ascribing this formula to the compounds of zirconium are as follows. In the first place, the investigation of the crystalline forms of the zirconofluorides—for example, K_2ZrF_6, $MgZrF_6,5H_2O$—which proved to be analogous in composition and crystalline form with the corresponding compounds of titanium, tin, and silicon. In the second place, the specific heat of Zr is 0·067, which corresponds with the atomic weight 90. The third and most important reason for doubling the combining weight of zirconium was given by Deville's determination of the vapour density of **zirconium chloride**, $ZrCl_4$. This substance is obtained by igniting zirconium oxide mixed with charcoal in a stream of dry chlorine, and is a colourless saline substance which is easily distilled at 440°. Its density referred to air was found to be 8·15, that is, 117 in relation to hydrogen, as it should be according to the molecular formula of this substance above cited. It exhibits, however, in many respect a saline character and that of an acid chloranhydride, for zirconium oxide itself presents very feebly developed acid properties but clearly marked basic properties. Thus zirconium chloride dissolves in water, and on evaporation the solution only partially disengages hydrochloric acid—resembling magnesium chloride, for example. Zirconium was discovered and characterised as an individual element by Klaproth.

Pure compounds of zirconium are generally prepared from zircon, which is finely ground; but as it is very hard it is first heated and thrown into cold water, by which means it is disintegrated. Zircon is decomposed or dissolved when fused with acid potassium sulphate, or still more easily when fused with acid potassium fluoride (a double soluble salt, K_2ZrF_6, is then formed); however, zirconium compounds are generally prepared from powdered zircon by fusing it with sodium carbonate and then boiling in water. An insoluble white residue is obtained consisting of a compound of the oxides of sodium and zirconium, which is then treated with hydrochloric acid and the solution evaporated to dryness. The silica is thus converted into an insoluble form, and zirconium chloride obtained in solution. Ammonia precipitates **zirconium** and Troost, by the action of aluminium on potassium zirconofluoride in the same way that silicon is prepared; it forms a crystalline powder, similar in appearance to graphite and antimony, but having a very considerable hardness, not much lustre, and a sp. gr. 4·15. In many respects it resembles silicon; it does not fuse when heated, and even oxidises with difficulty, but liberates hydrogen when fused with potash. When fused with silica it liberates silicon. With carbon in the electric furnace it forms ZrC_2 and with hydrogen it gives ZrH_2 (Winkler); hydrochloric and nitric acids act feebly on it, but aqua regia easily dissolves it. It is distinguished from silicon by the fact that hydrofluoric acid acts on it with great facility, even in the cold and when diluted, whilst this acid does not act on silicon at all.

The very similar element **thorium** ($Th=232$) was distinguished by Berzelius (1828) from zirconium. It is met with in the very rare *thorite* and *orangeite*, $ThSiO_4,2H_2O$ (sp. gr. 4·8), and also in the cerite and gadolinite earths, especially in monazite, which is a phosphate of cerium, $CePO_4$, in which a portion of the oxide of cerium is replaced by the oxides of other rare earths, including thorium (see Chap. XVII.; Brauner). The monazite of Carolina contains as much as 4 per cent. of ThO_2.[59] Although oxide of thorium resembles the oxides R_2O_3

---

hydroxide from this solution, as a white gelatinous precipitate, $ZrO(OH)_2$. When ignited, this hydroxide loses water and in so doing undergoes spontaneous recalescence and leaves a white infusible and exceedingly hard mass of **zirconium oxide**, ZrO_2, having a specific gravity of 5·4 (in the electric furnace, ZrO_2 fuses and volatilises like SiO_2—Moissan). Owing to its infusibility, zirconium oxide is used as a substitute for lime and magnesia in the Drummond light. This oxide, in contradistinction to titanium oxide, is soluble, even after prolonged ignition, in hot strong sulphuric acid. The hydroxide is readily soluble in acids. The composition of the salts is ZrX_4, or $ZrOX_2$ or $ZrOX_2,ZrO_2$, just as with those of its analogues. But although zirconium oxide forms salts in the same way with acids, it also gives salts with bases. Thus, it liberates carbonic anhydride when fused with sodium carbonate, forming the salts $Zr(NaO)_4$, $ZrO(NaO)_2$, &c. Water, however, destroys these salts and extracts the soda.

[59] ThO_2 is obtained by heating finely powdered thorite with sulphuric acid and precipitating the solution (after treating with H_2S) with alkali. The resultant hydrate, $Th(OH)_4$, is then dissolved in acid, re-precipitated with oxalic acid, and ignited. The oxide is purified by converting it into sulphate, which is soluble (in an anhydrous form, after heating to 450°) in ice-cold water. The solution, like those of the sulphates of all the 'rare earths,' when heated deposits a portion of its salt in crystals, having the composition $Th(SO_4)_2,9H_2O$. A very pure salt may be obtained by repeating this process several times. In treating monazite, the majority of the cerite earths are separated by taking advantage either of the fact that the precipitated sodium oxalate salt is easily soluble in a solution of the ammonium oxalate salt (like the salts of ytterbium), but is precipitated from solutions strongly acidulated with sulphuric acid (the salt of Yb_2O_3 then remains in solution) or the double ammonium oxalate is treated with an excess of nitric acid, in which case the thorium salt is precipitated and the accompanying metals remain in solution, or else other more complex methods are employed, based on the fact that the thorium salt of hydrazoic acid, HN_3, is insoluble. The treatment of thorite, and especially of monazite, is carried out on a large scale for preparing the nitrate, $Th(NO_3)_4$ (crystallising with 12 or 6 or $5H_2O$) which is used in the mantles of the Auër

of the 'rare earths' (cerite and gadolinite),[60] and exhibits feebly basic properties, yet it undoubtedly belongs to the oxides RO_2, not only because of its isomorphism with the compounds of Ti and Zr (Delafontaine, 1863) and the atomic weight of about 232–233 (if the oxide have the composition ThO_2, of which there can be no doubt), but also from the vapour density of the difficultly volatile chloride $ThCl_4$ (obtained by heating a mixture of ThO_2 and carbon in a stream of chlorine and also by other methods) and the specific heat of the metal (0·028), obtained by fusing the double salt of KCl and $ThCl_4$ with sodium and having a sp. gr. of about 11·1, according to Clève, Nilson, and Krüss.[61] The salts of oxide of thorium, ThX_4, are colourless, give no absorption spectrum, and as salts of a feeble base easily give $ThOX_2$.

---

v. Welsbach incandescent burners. The idea of these burners originally came from Bunsen, who observed that the 'rare earths,' and especially the oxide of erbium, emit a brilliant light when heated. A mixture of ThO_2 with 1 per cent. of CeO_2 is now used for this purpose. The network mantle is soaked in a solution of the nitrates of these metals and calcined. A skeleton of the oxides then remains in the place of the net, and is used for giving an incandescent light in a smokeless flame of a gas or kerosene burner (Bunsen). This gives a most brilliant and also economical light.

[60] Like the oxides R_2O_3 of the rare metals, oxide of thorium, ThO_2, in the form of its salts, ThX_4, gives with alkalies a precipitate of the colourless hydrate, $Th(OH)_4$. The precipitate given by oxalic acid is insoluble in feeble acids, just as with the cerite oxides, and the double sulphate is also insoluble in a saturated solution of K_2SO_4. But the precipitate of the cerite salts with Na_2CO_3 is not soluble in an excess of the reagent, whilst that of ThX_4 is soluble. The precipitate given by oxalic acid is soluble in a solution of ammonium oxalate. Peroxide of hydrogen (in a neutral solution at 60°) precipitates the salts of ThO_2 with great ease, as I am told by Prof. Brauner, who has devoted much labour to the investigation of thorium, and has shown that it usually contains small amounts of another metal which has not yet been separated but which undoubtedly lowers its atomic weight. This also agrees with the results of other recent but not yet completed researches, which have been incited by the radio-activity of the native compounds of thorium (see Chap. XXI., note 15a).

[61] Nilson and Clève, Brauner, Moissan and Étard, Krüss, Matthews, Haber, Wyrouboff, Pissarjeffsky (who investigated the peroxides formed by the action of H_2O_2), and others obtained and investigated many compounds of thorium and showed the great interest attaching to some of its derivatives, but this is not the place to enlarge upon them.

CHAPTER XIX

PHOSPHORUS AND OTHER ELEMENTS OF THE FIFTH GROUP

NITROGEN is the lightest as well as the typical and most widely distributed representative of the elements of the fifth group, which form a higher saline oxide of the form R_2O_5 and a hydrogen compound of the form RH_3. Phosphorus, arsenic, bismuth, and antimony belong to the uneven series of this group. **Phosphorus** is the most widely distributed of these elements. There is hardly any mineral substance composing the mass of the earth's crust which does not contain some—though perhaps a small—amount of the salts of phosphoric acid. The soil and earthy substances in general usually contain from one to ten parts of phosphoric acid in 10,000 parts. This amount, which appears so small, has, however, a very important significance in nature. No plant can attain its natural growth if it be planted in an artificial soil completely free from phosphoric acid. Plants equally require the presence of salts of potassium, magnesium, calcium, and iron, among basic oxides, and of carbonic, sulphuric, nitric, and phosphoric anhydrides, among acid oxides. In order to increase the fertility of a more or less poor soil, the above-named nutritive elements are introduced into it by means of fertilisers. Direct experiment has proved that these substances are undoubtedly necessary to plants, but that they must be all present simultaneously and in small quantities, and that an excess, like an insufficiency, of one of these elements is necessarily followed by a bad harvest, or an imperfect growth, even if all the other conditions (light, heat, water, air) are normal. The phosphoric compounds of the soil accumulated by plants pass into the animal organism, in which these substances are assimilated in many instances in large quantities. Thus the chief component part of bones is calcium phosphate, $Ca_3P_2O_8$, and it is on this that their hardness depends.[1]

---

[1] Dry bones consist of about one-third of gelatinous matter and about two-thirds of ash, chiefly calcium phosphate. The salts of phosphoric acid are also found in the mass of the earth as separate minerals; for example, the **apatites** contain this salt in a crystalline form, combined with calcium chloride or fluoride, $CaR_2,3Ca_3(PO_4)_2$ (where $R=F$ or Cl), the two being sometimes in a state of isomorphous mixture. This mineral often crystallises in fine hexagonal prisms of sp. gr. 3·17 to 3·22. Vivianite is a hydrated

Phosphorus was first extracted by Brand in 1669 by the ignition of evaporated urine. After the lapse of a century, Scheele, who knew of the existence of a more abundant source of phosphorus in bones, pointed out the method which is now employed for the extraction of this element. Calcium phosphate in bones permeates a nitrogenous organic substance, which is called ossein, and forms a jelly. When bones are treated exclusively for the extraction of phosphorus, neglecting the gelatin, they are burnt, in which case all the ossein is burnt away. When, however, it is desired to preserve the gelatin, the bones are immersed in cold dilute hydrochloric acid, which dissolves the calcium phosphate and leaves the gelatin untouched; calcium chloride and acid calcium phosphate, $CaH_4(PO_4)_2$, are then obtained in the solution. When the bones are burnt directly in an open fire, their mineral components only are left as an ash, containing about 90 per cent. of calcium phosphate, $Ca_3(PO_4)_2$, mixed with a small amount of calcium carbonate and other salts. This mass is treated with sulphuric acid, and then the soluble acid calcium phosphate passes also into solution.

$$Ca_3(PO_4)_2+2H_2SO_4=2CaSO_4+CaH_4(PO_4)_2.$$
$$Ca_3(PO_4)_2+4HCl=2CaCl_2+CaH_4(PO_4)_2.$$

On evaporating the solution, the acid calcium phosphate crystallises out. The extraction of the phosphorus from $CaH_4(PO_4)_2$ consists in **heating it with charcoal** to a white heat. When heated, the acid phosphate, $CaH_4(PO_4)_2$, first parts with water, and forms the metaphosphate, $Ca(PO_3)_2$, which for the sake of simplicity may be regarded, like the acid salt, as composed of pyrophosphate and phosphoric anhydride, $2Ca(PO_3)_2=Ca_2P_2O_7+P_2O_5$. The latter, with charcoal, gives phosphorus and carbonic oxide, $P_2O_5+5C=P_2+5CO$. So that in reality a somewhat complicated reaction here takes place according to the following equation:

$$2CaH_4(PO_4)_2+5C=4H_2O+Ca_2P_2O_7+P_2+5CO.$$

After the steam has come over, phosphorus and carbonic oxide distil

---

ferrous phosphate, $Fe_3(PO_4)_2,8H_2O$. Phosphates of copper are frequently found in copper mines; for example, *tagilite*, $Cu_3(PO_4)_2,Cu(OH)_2,2H_2O$. Lead and aluminium form similar salts. They are nearly all insoluble in water. The turquoise, for instance, is hydrated phosphate of alumina, $(Al_2O_3)_2,P_2O_5,5H_2O$, coloured with a salt of copper. Sea and other waters always contain a small amount of phosphates, and, indeed, the ash of sea plants, as well as that of land plants, always contains phosphates. Deposits of calcium phosphate are often met with; they are termed **phosphorites** and *osteolites*, and are composed of the fossil remains of the bones of animals; they are used for manure. Of the same nature are the so-called guano deposits from Baker's Island, and entire strata met with in Spain, France, and the United States, and in the governments of Orloff and Kursk in Russia. It is evident that if a soil destined for cultivation contain very little phosphoric acid, the fertilisation by means of these minerals will be beneficial, but, naturally, only if the other elements necessary to plants be present in the soil.

over from the retort and calcium pyrophosphate remains behind.[1a] As this reaction requires a white heat the retorts are soon worn out, so that ahe preparation of phosphorus is now carried on in furnaces in which the temperature is raised to the necessary degree by passing an electric current between carbon electrodes the charge of phosphorites or burnt bones, carbon, and sand being melted in the voltaic arc: $Ca_3P_2O_8 + 5C + 3SiO_2 = 3CaSiO_3 + 5CO + 2P$. The silicate fuses and the phosphorus distils over completely.[1b]

As phosphorus melts at about 40°, it condenses in the receiver in a molten liquid mass, which is cast under water in moulds, and is sold in the form of sticks or discs. This is common or **yellow phosphorus.** It is a transparent, yellowish or colourless waxy substance, which is not brittle, is almost insoluble in water, and easily undergoes change in its external appearance and properties under the action of light, heat, and of various substances. It crystallises (by sublimation or from its solution in carbon bisulphide) in the regular system, and[2] (in

---

[1a] By subjecting the pyrophosphate to the action of sulphuric or hydrochloric acid, it is possible to obtain a fresh quantity of the acid salt from the residue, and in this manner to extract all the phosphorus. It is usual to take burnt bones; mineral phosphorites and apatites may also be employed as materials for the extraction of phosphorus for the manufacture of matches. A great many methods have been proposed for facilitating the extraction of phosphorus, but none of them differ essentially from the usual one, because the problem is dependent on the liberation of phosphoric acid by the action of acids, and on its ultimate reduction by charcoal. Thus the calcium phosphate may be mixed directly with charcoal and sand, and phosphorus will be liberated on heating the mixture, because the silica displaces the phosphoric anhydride, which gives carbonic oxide and phosphorus with the charcoal. It has also been proposed to pass hydrochloric acid over an incandescent mixture of calcium phosphate and charcoal; the acid then acts just as the silica does, liberating phosphoric anhydride, which is reduced by the charcoal. It is necessary to prevent the access of air in the condensation of the vapours of phosphorus, because they take fire very easily; hence they are condensed under water by causing the gaseous products to pass through a vessel full of water. For this purpose the condenser shown in fig. 94 is usually employed.

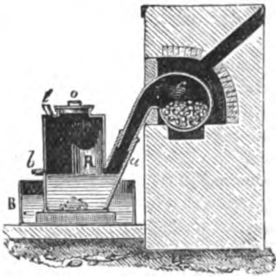


FIG. 94.—Preparation of phosphorus. The mixture is calcined in the retort *c*. The vapours of phosphorus pass through *a* into water without coming into contact with air. The phosphorus condenses in the water, and the gases accompanying it escape through *t*.

[1b] It has also been proposed to combine the extraction of phosphorus in the electric furnace with the manufacture of calcium carbide, CaC_2, by the addition of lime to the charge.

[2] Vernon (1891) states that ordinary (yellow) phosphorus is dimorphous. If it is melted and by careful cooling brought in a liquid form to as low a temperature as possible, it gives a variety which melts at 45·3° (the ordinary variety fuses at 44·3°), has the sp. gr. 1·827 (that of the ordinary variety is 1·818) at 13°, and crystallises in rhombic prisms (instead of in forms belonging to the cubic system). This is similar to the relation between octahedral and prismatic sulphur (Chap. XX.).

contradistinction to the other varieties) is easily soluble in carbon bisulphide, and also to some extent in other oily liquids. In this it recalls common sulphur. Its specific gravity is 1·84. It fuses at 44° (the melting-point rises rapidly with the pressure, and, according to Tammann, is about 100° at a pressure of 2,100 atmospheres), and passes into vapour at 290° (at 220° under a pressure of ½ atmosphere; at 360° the vapour pressure is 3·2 atmospheres; and at 440°, 7·5 atmospheres); it is easily inflammable, and must therefore be handled with great caution; careless rubbing is enough to cause phosphorus to ignite. Its application in the manufacture of matches is based on this.[2a] It emits light in the air owing to its slow [3] oxidation, and is therefore kept under water (such water is phosphorescent in the dark, like phosphorus itself). It is also very easily oxidised by various oxidising agents and takes up the oxygen from many substances.[3a] Phosphorus enters into direct combination with many metals and with sulphur,

---

[2a] According to Herr Irinyi (a Hungarian student), the first phosphorus matches were made in Austria at Roemer's works in 1837.

[3] The absorption of the oxygen of the atmosphere at the ordinary temperature by a large surface of phosphorus proceeds so uniformly, regularly, and rapidly that it may serve, as Ikeda (Tokio, 1893) has shown, for demonstrating the law of the velocity (rate) of reaction, which is considered in theoretical chemistry, and states that the rate of reaction is proportional to the active mass of a substance—i.e., $dx/dt = k(A - x)$, where t is the time, A the initial mass of the reacting substance (in this case oxygen), x the amount of it which has entered into reaction, and k the coefficient of proportionality. Ikeda took a test-tube (diameter about 10 mm.) and covered its outer surface with a coating of phosphorus (by melting it in a test-tube of large diameter, inserting the smaller test-tube, and, when the phosphorus had solidified, breaking away the outer test-tube), and introduced it into a definite volume of air, contained in a Woulfe's bottle (immersed in a water-bath to maintain a constant temperature), one of whose orifices was connected with a mercury manometer showing the fall of pressure, x. Knowing that the initial partial pressure of the oxygen (in air about 750 × 0·209) was about 155 mm. = A, the coefficient of the rate of reaction, k, is given from the law of the variation of the rate of reaction with the mass of the reacting substance, by the equation: $k = \frac{1}{t} \log \frac{A}{A - x}$, where t is the time, counting from the commencement of the experiment, in minutes. When the surface of the phosphorus was about 11 sq. cm., the following results were actually obtained:

$t = 10$	20	30	40	50	60 minutes
$x = 10·5$	21·5	31·1	40·7	49·1	57·3 mm.
$10,000\ k = 32$	32	32	33	33	33

The constancy of k is well shown in this case. The determination takes a comparatively short time, so that it may serve as a lecture experiment, and demonstrates one of the most important laws of chemical mechanics.

[3a] Not only do oxidising agents like nitric, chromic, and similar acids act upon phosphorus, but even the alkalies are attacked—that is, phosphorus acts as a reducing agent. In fact it reduces many oxides; thus, for instance, it liberates copper from its salts. When phosphorus is heated with sodium carbonate, the latter is partially reduced to carbon. If phosphorus be placed under water slightly warmed, and a stream of oxygen be passed over it, it will burn under the water.

chlorine, &c., with development of a considerable amount of heat. It is very poisonous, although scarcely soluble in water.

Besides this, there is a red variety of phosphorus, which differs considerably from the above. **Red phosphorus** (sometimes wrongly called amorphous phosphorus) is partially formed when ordinary phosphorus remains exposed to the action of light for a long time. It is also formed in many reactions; for example, when ordinary phosphorus combines with chlorine, bromine, or oxygen, a portion of it is converted into red phosphorus. A small quantity of iodine (or selenium) is able to convert (by mere contact, as the transformation of white into red phosphorus is accompanied by the evolution of heat) a large amount of ordinary phosphorus (fused or dissolved in CS_2) into the red variety. Schrötter in Vienna (1845) investigated this variety of phosphorus, and pointed out by what methods it may be produced in considerable quantities below 250°. The conversion of ordinary into red phosphorus proceeds still more rapidly at about 500° (and therefore under a somewhat increased vapour pressure in a closed vessel). Red phosphorus is a powdery reddish-brown opaque substance of specific gravity 2·14. It does not combine so energetically with oxygen and other substances as yellow phosphorus, and evolves less heat in combining with them.[4]

---

[4] The thermochemical determinations for phosphorus and its compounds date from the last century, when Lavoisier and Laplace burnt phosphorus in oxygen in an ice calorimeter. Andrews, Despretz, Favre, and others have also studied the subject. The most accurate and complete data are due to Thomsen. To determine the heat of combustion of yellow phosphorus, Thomsen oxidised it in a calorimeter with iodic acid in the presence of water, and a mixture of phosphorous and phosphoric acids was thus formed, the iodic acid being converted into hydriodic acid. It was first necessary to introduce two corrections into the calorimetric result obtained, one for the oxidation of the phosphorous into phosphoric acid, knowing their relative amounts by analysis, and the other for the deoxidation of the iodic acid. The result then obtained expresses the conversion of phosphorus into hydrated phosphoric acid. This must be corrected for the heat of solution of the hydrate in water, and for the heat of combination of the anhydride with water, before we can obtain the heat evolved in the reaction of P_2 with O_5 in the formation of P_2O_5. It is natural that with so complex a method there is a possibility of many small errors, and the resultant figures will only present a certain degree of accuracy after repeated corrections by various methods. Of such a kind are the following figures determined by Thomsen, which we express in thousands of calories:—$P_2 + O_5 = 370$; $P_2 + O_5 + 3H_2O = 400$; $P_2 + O_5 +$ a mass of water $= 405$. Hence we see that $P_2O_5 + 3H_2O = 30$; $2PH_3O_4 +$ an excess of water $= 5$. Experiment further showed that crystallised PH_3O_4, in dissolving in water, evolves 2·7 thousand calories, and that fused (39°) PH_3O_4 evolves 5·2 thousand calories, whence the heat of fusion of $H_3PO_4 = 2·5$ thousand calories. For phosphorous acid, H_3PO_3, Thomsen obtained $P_2 + O_3 + 3H_2O = 250$, and the solution of crystallised H_3PO_3 in water $= -0·13$, and that of fused $H_3PO_3 = +2·9$. For hypophosphorous acid, H_3PO_2, the heats of solution are nearly the same ($-0·17$ and $+2·1$), and the heat of formation, $P_2 + O + 3H_2O = 75$; hence its conversion into $2H_3PO_3$ evolves 175 thousand calories, and the conversion of $2H_3PO_3$ into $2H_3PO_4$, 150 thousand calories. For the sake of comparison we will take the combination of chlorine with phosphorus, also according to Thomsen, per 2 atoms of phosphorus: $P_2 + 3Cl_2 = 151$,

Common phosphorus easily oxidises in the air; red phosphorus does not oxidise at all at the ordinary temperature; hence it does not phosphoresce in the air, and may be very conveniently kept in the form of powder. It does not, like yellow phosphorus, fuse at 44°, but at 360°. After being converted into vapour at 290° or 300°, it again passes into the ordinary variety when slowly cooled. The vapour pressure is much below that of ordinary phosphorus, being about 0·1 atmosphere at 360°, whilst that of yellow phosphorus is 3·2 atmospheres and at 500° the vapour pressures are 9 and about 20 atmospheres respectively.[4a] Red phosphorus is not soluble in carbon bisulphide and other oily liquids, which permits of its being freed from any admixture of the ordinary phosphorus. It is not poisonous, and is used in many cases for which the ordinary phosphorus is unsuitable or dangerous; for example, in the manufacture of matches, which are then not poisonous or inflammable by accidental friction, so that here the red variety has now replaced the ordinary phosphorus.[4b]

The heads of the 'safety' matches do not contain any phosphorus, but only substances capable of burning and of supporting combustion. Red phosphorus is spread over a surface on the box, and it is the friction against this phosphorus which ignites the matches. There is no danger of the matches taking fire accidentally, nor are they poisonous.[5] This

---

$P_2 + 5Cl_2 = 210$ thousand calories. In their reaction on an excess of water (with the formation of a solution), $2PCl_3 = 130$, $2PCl_5 = 247$, and $2POCl_3 = 142$ thousand calories.

Besides which we shall cite the following data given by various observers: heat of fusion for P (that is, for 31 parts of phosphorus by weight) $-0·15$ thousand calories; the conversion of yellow into red phosphorus for P, from $+19$ to $+27$ thousand calories; $P + H_3 = 4·3$, $HI + PH_3 = 24$, $PH_3 + HBr = 22$ thousand calories.

[4a] Bakhius Roozeboom, Tammann, and others have expressed graphically the complex relations between the volume, temperature, and pressure for phosphorus. The student will find details of this subject in works on physical chemistry (the doctrine of phases).

[4b] Ordinary phosphorus takes fire at a temperature (60°) at which no other known substance will burn. Its application to the manufacture of matches is based on this property. In order to illustrate the great inflammability of common (yellow) phosphorus, its solution in carbon bisulphide may be poured over paper; this solvent quickly evaporates, and the free phosphorus spread over a large surface takes fire spontaneously, notwithstanding the cooling effect produced by the evaporation of the bisulphide. The majority of **phosphorus matches** are composed of common phosphorus mixed with some oxidising substance which easily gives up oxygen, such as lead dioxide, potassium chlorate, nitre, &c. For this purpose common phosphorus is carefully triturated under warm water containing a little gum; lead dioxide and potassium nitrate are then added to the resultant emulsion, and the match ends, previously coated with sulphur or paraffin, are dipped into this preparation. After this the matches are dipped into a solution of gum and shellac in order to preserve the phosphorus from the action of the air. When such a match containing particles of yellow phosphorus is rubbed over a rough surface, it becomes (especially at the point of rupture of the brittle gummy coating) slightly heated, and this is sufficient to cause the phosphorus to take fire and burn at the expense of the oxygen of the other ingredients.

[5] In the so-called 'safety' or Swedish matches a mixture of red phosphorus and glass

red phosphorus is prepared by heating ordinary phosphorus at 230° to 270° ; it is evident that this must be done in an atmosphere incapable of supporting combustion—for example, in nitrogen, carbonic anhydride, steam, &c. On a large scale, ordinary phosphorus is placed in closed iron vessels,[5a] and immersed in a bath of different proportions of tin and lead, by which means the temperature of 250°, necessary for the conversion, is easily attained. It is kept at this temperature for some time. The temperature is at first cautiously raised, and the air is thus partially expelled by the heat, and also by the evolution of steam (the phosphorus is damp when put in), while the remaining oxygen is also partially absorbed by the phosphorus, so that an atmosphere of nitrogen is produced in the iron vessel. Red phosphorus enters into all the reactions proper to yellow phosphorus, only with greater difficulty and more slowly ;[6] and, as its vapour pressure (volatility) is less than that

---

forms the surface on which the matches are struck, and the matches themselves do not contain any phosphorus at all, but a mixture of antimonious sulphide, Sb_2S_3 (or similar combustible substances) and potassium chlorate (or other oxidising agents). The combustion, when once started by contact with the red phosphorus, proceeds by itself at the expense of the inflammatory and combustible elements contained in the tip of the match. The mixture forming the heads of the 'safety' matches has the following approximate composition : 55–60 parts of chlorate of potassium, 5–10 parts of peroxide of manganese (or of $K_2Cr_2O_7$), about 1 part of sulphur or charcoal, about 1 part of pentasulphide of antimony, Sb_2S_5, and 30–40 parts of rouge and powdered glass. This mixture is stirred up in gum or glue, and the matches are dipped into it. The paper on which the matches are struck is coated with a mixture of red phosphorus and trisulphide of antimony, Sb_2S_3, stirred up in dextrine.

[5a] Phosphorus only acts on iron at a red heat. The boiler is provided with a safety valve and gas-conducting tube, which is immersed in mercury or other liquid to prevent the admission of air into the boiler.

[6] The specific heat of the yellow variety is 0·189, and is greater than that of the red variety, which is 0·170. The sp. gr. of the yellow form is 1·84, and that of the red prepared at 260°, 2·15, and of that prepared at 580° and above (i.e., 'metallic' phosphorus ; see below), 2·34. At 230° the pressure of the vapour of ordinary phosphorus is 514 millimetres of mercury, and of the red, 0—that is to say, red phosphorus does not form any vapour at this temperature ; at 447° the vapour pressure of ordinary phosphorus is at first 5,500 mm., but it gradually diminishes with the formation of red phosphorus, for which it is equal to 1,636 mm.

Hittorf, by heating the lower portion of a closed tube containing red phosphorus to 530° and the upper portion to 447°, obtained crystals of the so-called 'metallic' phosphorus at the upper extremity. As the vapour pressures (according to Hittorf, at 530° the vapour of yellow phosphorus is 8,040 mm., that of red, 6,139 mm., and that of metallic, 4,130 mm.) and reactions are different, **metallic phosphorus** may be regarded as a distinct variety. It is still less energetic in its chemical reactions than red phosphorus, and it is denser than the two preceding varieties, its sp. gr. being 2·34. It does not oxidise in the air, is crystalline, and has a metallic lustre. It is obtained when ordinary phosphorus is heated with lead for several hours at 400° in a closed vessel from which the air has been exhausted. The resultant mass is then treated with dilute nitric acid, which first dissolves the lead (phosphorus is electro-negative to lead, and does not therefore, act on the nitric acid at first) and leaves brilliant rhombohedral crystals of phosphorus of a dark-violet colour with a slight metallic lustre, which conduct an electric current incomparably better than the yellow variety; this also is characteristic of the yellow variety, it may be supposed that polymerisation takes place in the passage of the yellow into the red modification, just as in the passage of cyanogen into paracyanogen, or of cyanic acid into cyanuric acid (Chap. IX., notes 39a and 48).

The vapour of phosphorus is colourless; its density remains almost constant between 300° and 1,000° (Dumas, 1833; Mitscherlich, Deville and Troost, 1859, and others; it falls slightly as the temperature rises). Referred to hydrogen, it is 62, and therefore corresponds with a molecular weight of 124, i.e., the molecule of phosphorus in a state of vapour contains P_4. The reader will remember that the molecule

of the metallic state of phosphorus. However, metallic phosphorus may be a well-crystallised variety of the red modification.

The researches of Lemoine partially explain the passage of yellow (ordinary) phosphorus into the other varieties. He heated a closed glass globe, containing either ordinary or red phosphorus, in the vapour of sulphur (440°), and then determined the amount of the red and yellow varieties after various periods of time, by treating the mixture with carbon bisulphide. It appeared that after the lapse of a certain time a mixture of definite composition is obtained from both—that is, between the red and yellow varieties a state of equilibrium sets in like that of dissociation, or that observed in double decompositions. But at the same time, the progress of the transformation appeared to be dependent on the quantity of phosphorus taken relatively to the volume of the globe (i.e., upon the pressure). Neglecting the latter, we will cite as an example the amounts of the red phosphorus transformed into the ordinary, and of the ordinary not converted into red, per 30 grams of red or yellow taken per litre capacity of the globe, heated to 440°. When red phosphorus was taken, 4·75 grams of yellow phosphorus were formed after two hours, four grams after eight hours, three grams after twenty-four hours, and the last limit remained constant on further heating. When thirty grams of yellow phosphorus were taken, five grams remained unaltered after two hours, four grams after eight hours, and after twenty-four hours and more, three grams as before. Troost and Hautefeuille showed that liquid phosphorus in general changes more easily into the red than does phosphorus vapour, which, however, is able, although slowly, to deposit red phosphorus according to the relation between t and V.

The question presents itself as to whether phosphorus in a state of vapour is the ordinary or some other variety. Hittorf (1865) collected many data for the solution of this problem, which leave no doubt that (as experimental figures show) the density of the vapour of phosphorus is always the same, although the vapour pressure of the different varieties and their mixtures is very variable. This shows that the different varieties of phosphorus only occur in a liquid and a solid state. Strictly speaking, the vapour of phosphorus is a particular state of this substance, and the molecular formula P_4 refers only to it, and not to any other definite state of phosphorus. But the method of the depression of the freezing-point (Chap. VII.) showed that in a benzene solution, the fall of the freezing-point indicates for ordinary phosphorus a molecule P_4, judging by the determinations of Paterno and Nasini (1888), Hirtz (1890), and Beckmann (1891), who obtained for sulphur by the same method a molecular weight corresponding with S_6, in conformity with the vapour density. Further research in this direction will perhaps show the possibility of finding the molecular weight of red phosphorus, if a means be discovered for dissolving it without converting it into the yellow variety.

I think it will not be out of place here to draw the reader's attention to the fact that red phosphorus stands nearer to nitrogen, whose molecule is N_2, in its small inclination towards chemical reactions, although, judging by its small vapour pressure, it must be more complex than ordinary (yellow and white) phosphorus. The conception of polymerisation alone cannot therefore account for everything in this instance.

of nitrogen contains N_2, that of sulphur S_6 or S_2, and that of oxygen O_2 or O_3.

The chemical energy of phosphorus in a free state more nearly approaches that of sulphur than nitrogen. Phosphorus is combustible and inflames at 60° ; but having in the act of combination parted with a portion of its energy in the form of heat it becomes analogous to nitrogen, so long as there is no question of its reduction back again into phosphorus. Nitric acid is easily reduced to nitrogen, whilst phosphoric acid is reduced with very much greater difficulty. All the compounds of phosphorus are less volatile than those of nitrogen. Nitric acid, HNO_3, is easily distilled ; metaphosphoric acid, HPO_3, is generally said to be non-volatile; triethylamine, $N(C_2H_5)_3$, boils at 90°, and triethyl-phosphine, $P(C_2H_5)_3$, at 127°.

Phosphorus not only combines easily and directly with oxygen, but also with chlorine, bromine, iodine, sulphur, and with certain metals, and red phosphorus when heated combines with hydrogen also.[6a] Thus, for instance, when fused with sodium under naphtha, phosphorus gives the compound Na_3P_2. Zinc, absorbing the vapour of phosphorus, gives the phosphide Zn_3P_2 (sp. gr. 4·76) ; tin, SnP ; copper, Cu_2P ; and even platinum combines with phosphorus (PtP_2, sp. gr. 8·77).[6b] Iron, when combined with even a small quantity of phosphorus, becomes brittle.[7] Some of these compounds of phosphorus are obtained by the action of phosphorus on the solutions of metallic salts, and by the ignition of metallic oxides in the vapour of phosphorus, or by heating mixtures of

[6a] Retgers (see further on) showed this in 1894, and observed that As when heated, also combines with hydrogen. The flame of hydrogen gas is coloured green by the presence of the smallest trace of free phosphorus (carried in the vapour of water).

[6b] The capacity of mercury (Chap. XVI., note 25a) to give unstable compounds with nitrogen gives rise to the supposition that similar compounds exist with phosphorus also. Such a compound was obtained by Granger (1892) by heating mercury with iodide of phosphorus in a closed tube at 275°–300°. After removing the iodide of mercury formed, there remain fine rhombic crystals having a metallic lustre, and the composition Hg_3P_2. This compound is stable, does not alter at the ordinary temperature, and only decomposes at a red heat; when heated in air it burns with a flame. Nitric or hydrochloric acid does not act upon it, but it is easily decomposed by aqua regia.

[7] The metallic compounds of phosphorus possess a great chemical interest, because they show a transition from metallic alloys to the sulphides, halogen salts, and oxides, and on the other hand to the nitrides. Although there are already many fragmentary data on the subject, the interesting province of the metallic phosphides cannot yet be regarded as in any way generalised. The varied applications (phosphor-iron, phosphor-bronze, &c.), which the phosphides have recently acquired should give a strong incentive to the complete and detailed study of this subject, which would, in my opinion, help to the explanation of chemical relations, beginning with alloys (solutions) and ending with salts and the compounds of hydrogen (hydrides), because the phosphor-metals, as is proved by direct experiment, stand in the same relation to phosphoretted hydrogen as the sulphides do towards sulphuretted hydrogen, or as the metallic chlorides to hydrochloric acid.

phosphates with charcoal and metals. Phosphides do not exhibit the external properties of salts, which are so clearly seen in the chlorides and still distinctly observable in the sulphides. **The phosphides of the metals** of the alkalies and of the alkaline earths are even immediately and very easily decomposed by water, whereas this is found to be the case with only a very few sulphides, and still more rarely and indistinctly with the chlorides. We may take calcium phosphide as an example.[7a] Phosphorus is laid in a deep crucible, and covered with a clay plug, over which lime is strewn. At a red heat the vapours of phosphorus combine with the oxygen of the lime and form phosphoric anhydride, which forms a salt with another portion of the lime, while the liberated calcium combines with the phosphorus and forms calcium phosphide. Its composition is not quite certain ; it may be CaP (corresponding with liquid phosphoretted hydrogen). This substance is remarkable for the following reaction : if it is thrown into water—or, better still, a dilute solution of hydrochloric acid—bubbles of gas are evolved, which take fire spontaneously in the air and form white rings. This is owing to the fact that the liquid hydrogen phosphide, PH_2, is first formed, thus, $CaP+2HCl=CaCl_2+PH_2$, and this, owing to its instability, very easily splits up into the solid phosphide, P_2H, and the gaseous one PH_3 : $5PH_2=P_2H+3PH_3$;[7b] the latter corresponds with ammonia. The mixture of the gaseous and liquid phosphides takes fire spontaneously in the air, forming phosphoric acid. The same hydrogen phosphides are formed when water acts on sodium phosphide (Na_3P_2). A similar mixture of gaseous, liquid and solid phosphoretted hydrogen (Retgers, 1894) is formed by heating (in a glass tube) red phosphorus in a stream of dry hydrogen. Hence we see that there are **three compounds of phosphorus with hydrogen** : (1) The solid yellow phosphide, P_2H (more probably P_4H_2), is obtained by the action of strong hydrochloric acid on sodium phosphide ; it takes fire when struck or when heated to 175°. (2) The liquid, PH_2, or more correctly expressed as the molecule, P_2H_4, is a colourless liquid which takes fire spontaneously in the air, boils at 60°, is very unstable, and is easily decomposed (by light or hydrochloric acid) into the two other phosphides of hydrogen. It is prepared by passing the gases evolved by the action of water

---

[7a] Many other compounds of phosphorus are also capable of forming phosphoretted hydrogen. Thus BP also gives PH_3 (see Chap. XVII., note 12). The following is another easy method for preparing PH_3. A mixture of 1 part of zinc dust (fume) and 2 parts of red phosphorus is heated in an atmosphere of hydrogen (the mixture burns in air). Combination takes place, accompanied by a flash, and a grey mass of Zn_3P_2 is formed which gives PH_3 when treated with dilute H_2SO_4.

[7b] Moissan obtained a phosphide of calcium having the composition Ca_3P_2 by heating $Ca_3(PO_4)_2$ in the electric furnace with carbon. With water it gives PH_3 without forming PH_2.

on calcium phosphide through a freezing mixture.[8] And, lastly, (3), gaseous hydrogen phosphide, *phosphine*, PH_3, which is distinguished as being the most stable. It is a colourless gas, which does not take fire in the air. It has an odour of garlic, and is very poisonous. It resembles ammonia in certain of its properties.[8a] It is easily decomposed by heat, like ammonia, forming phosphorus and hydrogen ; but it is very slightly soluble in water, and does not saturate acids, although with some of them it forms compounds which resemble ammonium salts in their form and properties. Among them **phosphonium iodide**, PH_4I, analogous to ammonium iodide, is worthy of notice. This compound crystallises on sublimation in well-formed lustrous cubes. It does not, however, enter into those reactions of double decomposition which are proper to sal-ammoniac, because its saline properties are very feebly developed ; even water decomposes it. Phosphoretted hydrogen also combines, like ammonia, with certain chloranhydrides ; but they are decomposed by water, with the evolution of phosphine. Ogier (1880) showed that hydrochloric acid also combines with phosphine under a pressure of 20 atmospheres at +18°, and under the ordinary pressure at −35°, forming the crystalline phosphonium chloride, PH_4Cl, corresponding with sal-ammoniac. Hydrobromic acid does the same with greater ease, and hydriodic acid with still greater facility, forming phosphonium iodide, PH_4I,[9] which acts in many cases as a powerful reducing agent.

---

[8] Discovered by Thénard, the spontaneous inflammability of the hydride PH_2 in air is very remarkable, and it is particularly interesting that its analogues in composition, $P(C_2H_5)_2$ (the formula must be doubled) and $Zn(C_2H_5)_2$, also take fire spontaneously in air.

[8a] The analogy between PH_3 and NH_3 is particularly clear in the hydrocarbon derivatives. Just as NH_2R, NHR_2, and NR_3, where R is CH_3 and other hydrocarbon radicles, correspond with NH_3, so there exist similar compounds corresponding with PH_3. These compounds form a branch of organic chemistry. The action of PH_3 on a solution of Na or K in liquid NH_3 leads to the formation of $PNaH_2$ or PKH_2, resembling the amides of Na and K.

[9] The periodic law and direct experiment (the molecular weight) show that PH_3 is the normal compound of P and H, and that it is more simple than PH_2 or P_2H_4, just as methane, CH_4, is more simple than ethane, C_2H_6, whose empirical composition is CH_3. The formation of liquid phosphoretted hydrogen may be understood from the law of substitution. The univalent radicle of PH_3 is PH_2, and if it is combined with H in PH_3 it replaces H in liquid phosphoretted hydrogen, which thus gives P_2H_4. This substance corresponds with free amidogen (hydrazine), N_2H_4 (Chap. VI.). Probably P_2H_4 is able to combine with HI, and perhaps also with 2HI, or other molecules—that is, to give a substance corresponding to phosphonium iodide.

Phosphonium iodide, PH_4I, may be prepared, according to Baeyer, in large quantities in the following manner:—100 parts of phosphorus are dissolved in dry carbon bisulphide in a tubulated retort; when the mixture has cooled, 175 parts of iodine are added little by little, and the carbon bisulphide is then distilled off, this being done towards the end of the operation in a current of dry carbonic anhydride at a moderate temperature. The neck of the retort is then connected with a wide glass tube, and the

Phosphoretted hydrogen or **phosphine,** PH_3, is generally prepared by the action of caustic potash on phosphorus.[10] Small pieces of phosphorus are dropped into a flask containing a strong solution of caustic potash and heated. Potassium hypophosphite, H_2KPO_2, is then obtained in solution; gaseous phosphoretted hydrogen is evolved:

$$P_4 + 3KHO + 3H_2O = 3KH_2PO_2 + PH_3.$$

Liquid phosphoretted hydrogen (and free hydrogen) is also formed, together with the phosphine, so that the gaseous product, on escaping from the water into the air, takes fire spontaneously, forming beautiful white rings of phosphoric acid. In this experiment, as in that with calcium phosphide, it is the liquid, P_2H_4, that takes fire; but the phosphine ignited by it also burns, $PH_3 + O_4 = PH_3O_4$. The same phosphoretted hydrogen, PH_3, may be obtained pure, and not spontaneously combustible, by igniting the hydrates of phosphorous acid ($4PH_3O_3 = PH_3 + 3PH_3O_4$) and hypophosphorous acid ($2PH_3O_2 = PH_3 + PH_3O_4$); or, more simply, by the decomposition of calcium phosphide by hydrochloric acid, because then all the liquid phosphide,

---

tubulure fitted with a funnel furnished with a stopcock and containing 50 parts of water. This water is added drop by drop to the phosphorous iodide, and a violent reaction takes place, with the evolution of hydriodic acid and phosphonium iodide. The latter collects as crystals in the glass tube and in the retort itself. It is purified by further distillations; more than 100 parts may be obtained. Baeyer expresses the reaction by the equation, $P_2I + 2H_2O = PH_4I + PO_2$; and the compound PO_2 may be represented as phosphorous phosphoric anhydride: $P_2O_5 + P_2O_3 = 4PO_2$. As a better proportion we may take 400 grams of phosphorus, 680 grams of iodine, and 240 grams of water, and express the formation thus: $13P + 9I + 21H_2O = 3H_4P_2O_7 + 7PH_4I + 2HI$ (Chap. XI., note 77).

Phosphonium iodide and even phosphine act as reducing agents in solutions of many metallic salts. Cavazzi showed that with a solution of sulphurous anhydride phosphine gives sulphur and phosphoric acid. At a red heat steam acts upon phosphorus according to the equation, $2P + 3H_2O = PH_3O_2 + PH_3$.

[10] The air must first be expelled from the flask by hydrogen, or some other gas which will not support combustion, as otherwise an explosion might take place owing to the spontaneous inflammability of the phosphoretted hydrogen.

The combustion of phosphoretted hydrogen in oxygen also takes place under water when the bubbles of both gases meet, and is very brilliant. The phosphoretted hydrogen obtained by the action of phosphorus on caustic potash always contains free hydrogen, and often even the greater part of the gas evolved consists of hydrogen. *Pure phosphoretted hydrogen* (not containing hydrogen or liquid or solid phosphides) is obtained by the action of a solution of potash on phosphonium iodide: $PH_4I + KHO = PH_3 + KI + H_2O$ (in just the same way as ammonia is liberated from ammonium chloride). The reaction proceeds easily, and the purity of the gas is seen from the fact that it is entirely absorbed by bleaching powder and is not spontaneously inflammable. Its mixture with oxygen explodes when the pressure is diminished (Chap. XVIII., note 5). The vapours of bromine, nitric acid, &c., cause it to again acquire the property of inflaming in the air; that is, they partially decompose it, forming the liquid hydride, P_2H_4. Oppenheim showed that when red phosphorus is heated at 200° with hydrochloric acid in a closed tube it forms the compound $PCl_3(H_3PO_3)$, together with phosphine.

P_2H_4, is decomposed into non-volatile P_2H and gaseous PH_3. Pure phosphine liquefies when cooled to −90°, boils at −85°, and solidifies at −135° (Olszewski). When phosphorus burns *in an excess*[10a] *of dry* oxygen, then only **phosphoric anhydride**, P_2O_5, is formed. It is prepared by dropping pieces of phosphorus through a wide tube, fixed into the upper neck of a large glass globe, on to a cup suspended in the centre of the globe. These lumps are set alight by touching them with a hot wire, and the phosphorus burns into P_2O_5. The dry air necessary for its combustion is forced into the globe through a lateral neck, and the white flakes of phosphoric anhydride formed are carried by the current of air through a second lateral neck into a series of Woulfe's bottles, where they settle as friable white flakes. Phosphoric anhydride may also be formed by passing dry air through a solution of phosphorus in carbon bisulphide. All the materials for the preparation of this substance must be carefully dried, because it **combines** with great eagerness **with water**, at the same time developing a large amount of heat and forming metaphosphoric acid, HPO_3, from which the water cannot be separated by heat. Phosphoric anhydride is a colourless snowlike substance, which attracts moisture from the air with the utmost avidity.

It fuses at a red heat, and then **volatilises** (it is therefore purified by distillation).[10b] Its affinity for water is so great that it takes it up from many substances. Thus, it converts sulphuric acid into sulphuric

---

[10a] If there is a deficiency of oxygen, **phosphorous anhydride**, P_2O_3, is formed. It was obtained by Thorpe and Tutton (1890) and is easily volatilised, melts at 22·5°, boils without change (in an atmosphere of N_2 or CO_2) at 173°, and is therefore easily separated from P_2O_5, which volatilises with difficulty. The vapour density shows that the molecular weight is double, i.e., P_4O_6 (like As_2O_3). Although colourless, phosphorous anhydride (its density in a state of fusion at 24° is 1·936) turns yellow and reddens in sunlight (possibly red phosphorus separates out ?), and decomposes at 400° forming hypophosphorous anhydride, P_2O_4 (note 11) and phosphorus. It passes into P_2O_5 in air or oxygen, and when slightly heated in oxygen becomes luminous, and ultimately takes fire. Cold water slowly transforms P_2O_3 into phosphoric acid, but hot water gives an explosion and leads to the formation of PH_3, ($P_4O_6 + 6H_2O = PH_3 + 3PH_3O_4$). Alkalies act in the same manner. It takes fire in chlorine and forms $POCl_3$ and PO_2Cl, and combines with sulphur at 160°, forming $P_2S_2O_3$ (the molecular formula is double this), a substance which volatilises *in vacuo* and is decomposed by water into H_2S and phosphoric acid, i.e., it may be regarded as P_2O_5, in which O_2 has been replaced by two atoms of sulphur. Judging from the above, the mixture of P_2O_3 and P_2O_5 formed in the combustion of phosphorus in air is transformed into P_2O_5 in an excess of oxygen.

[10b] Phosphoric anhydride, P_2O_5, is obtained in a crystalline form when carefully distilled (in an atmosphere of CO_2), and it then boils at 250°. But with the amorphous variety (which is easily and generally formed, especially at 400°) the vapour pressure is very small at 250° (Hautefeuille), and in this form the anhydride, fused at a red heat, solidifies into a vitreous mass, which cracks after being kept some time, and which combines less vigorously with water than the crystalline form. The vitreous modification, however, also passes into the crystalline variety when distilled. This is probably another instance of polymerisation like that we shall presently meet with in metaphosphoric acid.

anhydride, while carbohydrates (wood, paper) are carbonised and give up the elements of water when brought into contact with it.

When *moist* phosphorus slowly oxidises in the air, it not only forms phosphorous and phosphoric acids, but also **hypophosphoric acid,** $H_4P_2O_6$, which when in a dry state easily splits up at 60° into phosphorous and metaphosphoric acids ($H_4P_2O_6 = H_3PO_3 + HPO_3$), but differs from a mixture of these acids in that it forms well-characterised salts, of which the sodium salt, $H_2Na_2P_2O_6$, is but slightly soluble in water (the sodium salts of phosphoric and phosphorous acids are easily soluble), and does not act as a reducing agent, like mixtures containing phosphorous acid.[11]

Judging by the general law of the formation of acids (Chap. XV.), the series of phosphorus compounds should include the following **ortho-acids** and their corresponding anhydrides, answering to phosphoretted hydrogen, H_3P :—

H_3PO_4, phosphoric acid, and P_2O_5, anhydride,
H_3PO_3, phosphorous acid, and P_2O_3, anhydride,
H_3PO_2, hypophosphorous acid, and P_2O, anhydride.[12]

---

[11] Salzer proved the existence of **hypophosphoric acid** (it is also called subphosphoric acid), in which many chemists did not believe. Drave (1888) and Rammelsberg (1892) investigated its salts. It may be obtained in a free state by the following method. The solution of acid produced by the slow oxidation of moist phosphorus is mixed with a solution (25 per cent.) of sodium acetate. A salt, $Na_2H_2P_2O_6,6H_2O$, crystallises out on cooling; it is soluble in 45 parts of water, and gives a precipitate of $Pb_2P_2O_6$ with lead salts ($Ag_4P_2O_6$ with salts of silver). The lead salt is decomposed by a current of hydrogen sulphide, when lead sulphide is precipitated, while the solution, evaporated under the receiver of an air-pump, gives crystals of $H_4P_2O_6,2H_2O$, which readily lose water and give $H_4P_2O_6$. The salts in which the H_4 is replaced by Ni_2, or $NiNa_2$, or $CdNa_2$, &c., are insoluble in water.

In order to see the relation between phosphoric acid and hypophosphoric acid, which does not contain the elements of phosphorous acid (because it does not reduce either gold or mercury from their solutions) but which nevertheless is capable of being oxidised (for example, by potassium permanganate) into phosphoric acid, it is simplest to apply the law of substitution. This clearly indicates the relation between oxalic acid, $(COOH)_2$, and carbonic acid, $OH(COOH)$. The relation between the above acids is exactly the same if we express phosphoric acid as $OH(POO_2H_2)$, because in this case $P_2H_4O_6$, or $(POO_2H_2)_2$, will correspond with it just as oxalic does with carbonic acid. A similar relationship exists between hyposulphuric or dithionic acid, $(SO_2OH)_2$, and sulphuric acid, $OH(SO_2OH)$, as we shall find in the following chapter. Dithionic acid corresponds with the anhydride S_2O_5, intermediate between SO_2 and SO_3; oxalic acid with C_2O_3, intermediate between CO and CO_2; hypophosphoric acid corresponds with the anhydride P_2O_4, which is intermediate between P_2O_3 and P_2O_5, and is the analogue of N_2O_4.

[12] Besides the hydrates enumerated, a compound, PH_3O, should correspond with PH_3. This hydrate, which is analogous to hydroxylamine, is not known in a free state, but it is known as triethylphosphine oxide, $P(C_2H_5)_3O$, which is obtained by the oxidation of triethylphosphine, $P(C_2H_5)_3$. It must be observed that there may also be lower oxides of phosphorus corresponding with PH_3, like N_2O and NO, and there are even indications of the formation of such compounds, but the data concerning them cannot be considered to be firmly established. Among the lower oxygen compounds of phosphorus, the **suboxide**

All these substances are known in a free state, and the types (but not the physical properties, owing to their being polymerised; for instance P_2O_3 gives a molecule P_4O_6, note 10a) of the anhydrides correspond to those of nitrogen, N_2O_5 (nitric anhydride), N_2O_3 (nitrous) and N_2O (hyponitrous),[12a] while the hydrates in their normal state contain more water than the corresponding nitrogen compounds and are orthohydrates containing as much hydrogen as the higher hydrogen compound, whereas the metahydrates for nitrogen are equal to orthohydrates less one molecule of water. However, phosphoric anhydride (P_2O_5) with a small quantity of water does not at first give orthophosphoric acid, PH_3O_4, but a compound P_2O_5,H_2O, or PHO_3, whose composition corresponds with that of nitric acid: this is **metaphosphoric acid.** Even with an excess of water, combining with phosphoric anhydride, this metaphosphoric acid, and not the ortho-compound, passes at first into solution. Metaphosphoric acid in solution only passes into orthophosphoric acid when the solution is heated or after a lapse of time.

Orthophosphoric acid[13] is obtained by oxidising phosphorus with nitric acid until the phosphorus passes entirely into solution and the lower oxides of nitrogen cease to be evolved. Red phosphorus is taken as a rule; if white phosphorus is used, the reaction takes place best with dilute nitric acid, and when aided by heat. The resultant solution is

---

P_4O obtained by Michaelis (1900) is of particularly frequent occurrence. It is formed in the oxidation of phosphorus, but usually together with the other oxides. It is obtained in a pure state by the action of acetic anhydride upon hypophosphorous acid by the elimination of water, phosphorous acid being also formed: $5PH_3O_2 = 6H_2O + PH_3O_3 + P_4O$. The same P_4O is formed if ordinary phosphorus is covered with a mixture of a 10 per cent. solution of NaHO with twice its volume of alcohol; hydrogen is then evolved and the phosphorus forms a dark-red solution, from which acids precipitate P_4O as a yellow powder of sp. gr. 1·9, which splits up into P_2O_5 and phosphorus when heated (in a state of dryness). It is redissolved by an alcoholic solution of NaHO, forming a red solution which gradually becomes colourless with the formation of hydrogen and hypophosphorous acid, $P_4O + 7H_2O = 4PH_3O_2 + H_2$, which proves the connection between P_4O and P_2O (note 12a). There is a solid phosphide of hydrogen, P_4H_2, corresponding with P_4O.

[12a] The compound P_2O, corresponding to hypophosphorous acid and N_2O, or **phosphorus dioxide,** was obtained by Besson (1897) by heating a mixture of PH_3O_3 and PCl_3, which leads first to the dehydration of the phosphorous acid and formation of P_2O_3, the latter then splitting up: $2P_2O_3 = P_2O_5 + P_2O$. The same substance is obtained by heating phosphonium bromide (note 9) with $POCl_3$ (note 13). Phosphorus dioxide forms a reddish-yellow powder which decomposes at 130°. Water has no action on it.

[13] Phosphoric acid, being a soluble and almost non-volatile substance, cannot be prepared, like hydrochloric and nitric acids, by the action of sulphuric acid on the alkali phosphates, although it is partially liberated in the process. For this purpose the phosphates of barium or lead may be taken, because they give insoluble precipitates; thus, $Ba_3(PO_4)_2 + 8H_2SO_4 = 3BaSO_4 + 2H_3PO_4$. Bone ash contains, besides calcium phosphate, sodium and magnesium phosphates, and fluorides and other salts, so that it cannot give directly a pure phosphoric acid.

evaporated to a syrup. If a weighed quantity of phosphorus be taken, a crystalline mass of the acid can be obtained by evaporating the solution until it consists only of the quantity[14] of phosphoric acid corresponding with the amount of phosphorus taken (from 31 parts of P, 98 parts of acid). The acid fuses at +39°, the specific gravity of the liquid being 1·88. Phosphorus pentachloride, PCl_5, and the oxychloride, $POCl_3$ (see further on), give orthophosphoric acid and hydrochloric acid with water. The two other varieties of phosphoric acid, with which we shall presently become acquainted, give the same ortho-acid under the influence of acids, with particular ease when boiled and more slowly in the cold. By itself, orthophosphoric acid (either in solution or when dry) does not pass into the other varieties; it does not oxidise, and therefore presents the limiting and stable form. When heated to 200°, it loses water and passes into pyrophosphoric acid, $2H_3PO_4 = H_2O + H_4P_2O_7$, whilst at an incipient red heat (about 350°) it loses twice as much water and is converted into metaphosphoric acid, $H_3PO_4 = H_2O + HPO_3$. In aqueous solution, orthophosphoric acid differs clearly from pyro- or meta-phosphoric acids, because the solutions of these latter acids give different reactions: thus, orthophosphoric acid does not precipitate albumin, does not give a precipitate with barium chloride, and forms a yellow precipitate of silver orthophosphate, Ag_3PO_4, with silver nitrate after being saturated with alkalies; whilst a solution of pyrophosphoric acid, $H_4P_2O_7$, although it does not precipitate albumin or barium chloride, gives a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$, with silver nitrate; and a solution of metaphosphoric acid, HPO_3, precipitates both albumin and barium chloride, and gives a white precipitate of silver metaphosphate, $AgPO_3$, with silver nitrate. These points of distinction were studied by Graham, and are exceedingly instructive. They show that the solution of a substance does not determine the maximum of chemical combination with water, that solutions may contain various degrees of combination with water, and that there is a great difference between the water serving for solution and that entering into chemical combination. Graham's experiments also showed that the water whose removal or combination determines the difference between ortho-, meta-, and pyro-phosphoric acids differs

---

[14] If this is not done, the orthophosphoric acid, PH_3O_4, loses a portion of its water, and then, as with an excess of water, it does not crystallise.

Phosphorus and hence also its preparations, usually contain arsenic. It may be separated from solutions of phosphoric acid by sulphuretted hydrogen. This induced Fittica (1900) to assume that he had succeeded in partly converting phosphorus into arsenic. C. Winkler afterwards proved that this was only a repetition of the mistake which has often given rise to the notion of the elements being transmutable into each other. Such mistakes are likely often to recur in insufficiently careful researches.

distinctly from water of crystallisation, for he obtained the salts of ortho-, meta-, and pyro-phosphoric acids with water of crystallisation, and they differed in their reactions like the acids themselves. This water of crystallisation was expelled with greater ease than the water of constitution of the hydrates in question.[14a]

Orthophosphoric acid has a pleasant acid taste and a distinctly acid reaction; it is used as a medicine, and is not poisonous (phosphorous acid is poisonous). Alkalies, like sodium, potassium, and ammonium hydroxides, saturate the acid properties of phosphoric acid when taken in the ratio $2NaHO : H_3PO_4$—that is, when salts of the composition HNa_2PO_4 are formed. When taken in the ratio $NaHO : H_3PO_4$, a salt having an acid reaction is obtained, and with $3NaHO : H_3PO_4$—that is, when the salt Na_3PO_4 is formed—an alkaline reaction is obtained. Hence many chemists (Berzelius) even regarded the salts of composition R_2HPO_4 as normal, and considered phosphoric acid to be dibasic.[14b] Orthophosphoric acid is tribasic, because it contains three equivalents of hydrogen replaceable by metals, forming salts, such as NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. It is also tribasic, because with silver nitrate its soluble salts always give Ag_3PO_4,[15] a salt with three equivalents of

---

[14a] The difference between the reactions of ortho-, meta-, and pyro-phosphoric acids, established by Graham, is of such importance for the theory of hydrates and for explaining the nature of solutions, that in my opinion its influence upon chemical thought has been far from exhausted. At the present time many such instances are known both in organic (for instance, the difference between the reactions of the solutions of certain anhydrides and hydrates of acids) and inorganic chemistry (for example, the difference between the rose and purple cobalt compounds, Chap. XXII. &c.). They essentially recall the long known and generalised difference between C_2H_4 (ethylene), C_2H_6O (ethyl alcohol = ethylene + water), and $C_4H_{10}O$ (ethyl ether = 2 ethylene + water = 2 alcohol − water). The power of meta- and pyro-phosphoric acids to pass gradually into the ortho-acid in the presence of water and the converse transition with the elimination of water show that the differences between them are not so very deep. Experiment (Montemartini, 1902) shows that dilute solutions of the pyro-acid pass into the ortho-acid more slowly than strong solutions, and this apparently indicates that the transition takes place, so to say, without the reaction of the actual molecules of phosphoric acid. The metaphosphoric acid absorbs water more slowly than the pyro-acid. Solutions of the sodium salts are far more stable than those of the acids themselves.

[14b] Other indicators (Chap. III., note 50) give other results, as Berthelot and others discovered; but I consider that distinctions of this kind throw little light on the essence of the matter, and shall therefore not linger further on them.

[15] Silver orthophosphate, Ag_3PO_4, is yellow, of sp. gr. 7·32, and insoluble in water. When heated it fuses like silver chloride, and if kept fused for some length of time it gives a white pyrophosphate (the decomposition which causes this is not known). It is soluble in aqueous solutions of phosphoric, nitric or even acetic acid, of ammonia, and of many of its salts. If silver nitrate acts on a dimetallic orthophosphate—for instance, Na_2HPO_4—it still gives Ag_3PO_4, nitric acid being disengaged: $Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$. When alcohol is added to silver orthophosphate Ag_3PO_4, dissolved in syrupy phosphoric acid, it precipitates a white salt (the alcohol takes up the free phosphoric acid) having the composition Ag_2HPO_4, which is immediately decomposed by water into the normal salt and phosphoric acid.

silver, and because by double decomposition with barium chloride it forms a salt of the composition $Ba_3(PO_4)_2$, and silver and barium hardly ever give basic salts. The monometallic orthophosphates of the metals of the alkalies are slightly soluble in water, but the trimetallic salts, $R_3(PO_4)_2$ and even the di-salts $R_2H_2(PO_4)=R_2(HPO_4)_2$ are insoluble in water, but dissolve in feeble acids, such as phosphoric and acetic, because they then form soluble acid or monometallic salts, $RH_4(PO_4)_2$ or $R(H_2PO_4)_2$.[16]

Phosphoric anhydride, or any of its hydrates, when ignited with an excess of sodium hydroxide, carbonate, &c., forms **normal** or **trisodium orthophosphate,** Na_3PO_4, but when a solution of sodium carbonate is decomposed by orthophosphoric acid, only the salt Na_2HPO_4 is formed; and when an excess of sodium chloride is ignited with orthophosphoric acid, hydrochloric acid is evolved, and the acid salt H_2NaPO_4 alone is formed. These facts [16a] clearly indicate the small

---

[16] The researches of Thomsen showed that in very dilute aqueous solutions the majority of monobasic acids—nitric, acetic, hydrochloric, &c. (but hydrofluoric acid more and hydrocyanic less)—HX evolve the following amounts of heat (in thousands of calories) with caustic soda: $NaHO + 2HX = 14$; $NaHO + HX = 14$; $2NaHO + HX = 14$; that is, if n be a whole number, $nNaHO + HX = 14$ and $NaHO + nHX = 14$. Hence reaction here only takes place between one molecule of NaHO and one molecule of acid, and the remaining quantity of acid or alkali does not enter into the reaction. In the case of dibasic acids, H_2R'' (sulphuric, dithionic, oxalic, sulphuretted hydrogen, &c.), $NaHO + 2H_2R'' = 14$; $NaHO + H_2R'' = 14$; $2NaHO + H_2R'' = 28$; $nNaHO + H_2R'' = 28$; that is, with an excess of acid ($NaHO + 2H'_2R''$) 14 thousand units of heat are developed, and with an excess of alkali 28. When phosphoric acid is taken (but not all tribasic acids—for instance, not citric), the general character of the phenomenon is similar to the preceding, namely, $NaHO + 2H_3PO_4 = 14{\cdot}7$; $NaHO + H_3PO_4 = 14{\cdot}8$; $2NaHO + H_3PO_4 = 27{\cdot}1$; $3NaHO + H_3PO_4 = 34{\cdot}0$; $6NaHO + H_3PO_4 = 35{\cdot}3$; or, in general terms, $NaHO + nH_3PO_4 = 14$ (approximately) and $nNaHO + H_3PO_4 = 35$ and not 42, which shows a peculiarity of phosphoric acid, i.e., the third equivalent of hydrogen acts more feebly than the first two. It will be seen from the preceding figures that $H_3PO_4 + NaHO = 14{\cdot}8$; $NaH_2PO_4 + NaHO = 12{\cdot}3$; $Na_2HPO_4 + NaHO = 5{\cdot}9$; with $Na_3PO_4 + NaHO$, a very small amount of heat is evolved, as may be judged from the fact that $Na_3PO_4 + 3NaHO = 1{\cdot}3$, but still heat is evolved. It must be supposed that in acting on phosphoric acid in the presence of a large quantity of water, a certain portion of the sodium hydroxide remains as alkali uncombined with the acid. Thus, on increasing the mass of the alkali heat is still evolved, and a fresh interchange between Na and H takes place. Hence water shows a decomposing action on the alkali phosphates. Recent researches made by Berthelot and Louguinine have confirmed the above deductions made by me in the first edition (1871) of this work. At the present time views of this nature are somewhat generally accepted, although they are not sufficiently strictly applied in other cases. As regards PH_3O_4 it may be said that on the substitution of the first hydrogen this acid acts as a powerful acid (like HCl, HNO , H_2SO_4); on the substitution of the second hydrogen as a weaker acid (like an organic acid); and on the substitution of the third, as one of the weakest acids, for instance, like phenol, HCN, &c.

The trimetallic salts of the tri-equivalent bases (Fe_2O_3, Al_2O_3, &c.) of the composition $FePO_4$, $AlPO_4$, are worthy of attention, because they are distinguished by their comparative stability and extreme simplicity of composition.

[16a] And also the reactions given by different indicators (Chap. III., note 50), as was shown by Berthelot (see note 14b).

energy of phosphoric acid with respect to the formation of the trimetallic salt, which is seen further from the fact that the salt Na_3PO_4 has an alkaline reaction, decomposes in the presence of water and carbonic acid, forming Na_2HPO_4, corrodes glass vessels in which it is boiled or evaporated, just like solutions of the alkalies ; disengages, like them, ammonia from ammonium chloride, and crystallises from solutions, as $Na_3PO_4,12H_2O$, only in the presence of an excess of alkali. At 15° the crystals of this salt require five parts of water for solution ; they fuse at 77°.

Disodium orthophosphate, or common sodium phosphate, Na_2HPO_4, is more stable both in solution and in the solid state. As it is used in medicine and in dyeing, it is prepared in considerable quantities, most frequently from the impure phosphoric acid obtained by the action of sulphuric acid on bone ash. The solution thus formed—which contains, besides phosphoric and sulphuric acids, salts of sodium, calcium, and magnesium—is heated, and sodium carbonate added so long as carbonic anhydride is disengaged. A precipitate is formed containing the insoluble salts of magnesium and calcium, whilst the solution contains sodium phosphate, Na_2HPO_4, with a small quantity of other salts, from which it may be easily purified by crystallisation. At the ordinary temperature its solutions, especially in the presence of a small amount of sodium carbonate, give well-formed inclined prismatic crystals, $Na_2HPO_4,12H_2O$; when the crystals are deposited above 30° they only contain $7H_2O$. The former crystals even lose a portion of their water of crystallisation at the ordinary temperature (the salt effloresces), and form the second salt with $7H_2O$; whilst under the receiver of an air-pump and over sulphuric acid they also part with this water.[17] When ignited they lose the last molecule of water of constitution, and give sodium pyrophosphate, $Na_4P_2O_7$.

Monosodium orthophosphate, NaH_2PO_4, crystallises with one equivalent of water; its solution has an acid reaction. At 100° the salt loses only this water of crystallisation, but at about 200° it parts with all its water, forming the metaphosphate $NaPO_3$. It is prepared from ordinary sodium phosphate by adding phosphoric acid until the

---

[17] $Na_2HPO_4,12H_2O$ has a sp. gr. 1·53. Poggiale determined the solubility in 100 parts of water (1) of the anhydrous ortho-salt Na_2HPO_4, and (2) of the corresponding pyro-salt $Na_4P_2O_7$:—

	0°	20°	40°	80°	100°
(1)	1·5	11·1	30·9	81	108
(2)	3·2	6·2	13·5	30	40

At temperatures of 20° to 100° the ortho-salt is so very much less soluble that this difference alone is sufficient to indicate the deeply seated alteration in constitution which takes place in the passage from the ortho- to the pyro-salts.

solution does not give a precipitate with barium chloride, and then evaporating and crystallising the solution. The solution of this salt does not absorb carbonic anhydride, and does not give a precipitate with salts of calcium, barium, &c.[18]

[18] The **ammonium orthophosphates** resemble the sodium salts in many respects, but the instability of the di- and tri-metallic salts is seen in them still more clearly than in the sodium salts; thus $(NH_4)_3PO_4$, and even $(NH_4)_2HPO_4$, lose ammonia in the air (especially when heated, even in solutions); $NH_4H_2PO_4$ alone does not disengage ammonia and has an acid reaction. The crystals of the first salt contain $8H_2O$, and are only formed in the presence of an excess of ammonia; both the others are anhydrous, and may be obtained like the sodium salts. When ignited, these salts leave metaphosphoric acid behind; for example, $(NH_4)_2HPO_4 = 2NH_3 = H_2O + HPO_3$. Ammonia also enters into the composition of many double phosphates. **Ammonium sodium orthophosphate,** $NH_4NaHPO_4,4H_2O$, crystallises in large transparent crystals from a mixture of the solutions of disodium phosphate and ammonium chloride (in which case sodium chloride is obtained in the mother liquor), or, better still, from a solution of monosodium phosphate saturated with ammonia. It is also formed from the phosphates in urine when it ferments. This salt is frequently used in testing metallic compounds by the blow-pipe, because when ignited it leaves a vitreous metaphosphate, $NaPO_3$, which, like borax, dissolves metallic oxides, forming characteristically tinted glasses.

When a solution of trisodium phosphate is added to a solution of a magnesium salt it gives a white precipitate of the normal orthophosphate, $Mg_3(PO_4)_2,7H_2O$. If the trisodium salt be replaced by the ordinary salt, Na_2HPO_4, a precipitate is also formed, and $MgHPO_4,7H_2O$ is obtained. It might be thought that the normal salt, $Mg_3(PO_4)_2$, would be precipitated if disodium phosphate was added to ammonia and a salt of magnesium, but in reality **ammonium magnesium orthophosphate**, $MgNH_4PO_4,6H_2O$, is precipitated as a crystalline powder, which loses ammonia and water when ignited, and gives a pyrophosphate, $Mg_2P_2O_7$. This salt occurs in nature as the mineral *struvite*, and in various products of the changes of animal matter. If we consider that the above salt parts with ammonia with difficulty, and that the corresponding salt of sodium is not formed under the same conditions ($MgNaPO_4,9H_2O$ is obtained by the action of magnesia on disodium phosphate), and turn our attention to the fact that the salts of calcium and barium do not form double salts as easily as magnesium, remembering that the salts of magnesium in general easily form double ammonium salts, we are led to think that this salt is not really a normal, but an acid salt, corresponding with Na_2HPO_4, in which Na_2 is replaced by the equivalent group NH_3Mg.

The common normal **calcium phosphate**, $Ca_3(PO_4)_2$, occurs in minerals, in animals, especially in bones, and also probably in plants, although the ash of many portions of plants, as a rule, contains less lime than the formation of the normal salt requires. Thus, 100 parts of the ash (from 5,000 parts of grain) of rye grain contain 47·5 of phosphoric anhydride and only 2·7 of lime, and even the ash of the whole of the rye (including the straw) contains twice as much phosphoric anhydride as lime, and the normal salt contains almost equal weights of these substances. Only the ash of grasses, and especially of clover, and of trees, contains in the majority of cases more lime than is required for the formation of $Ca_3P_2O_8$. This salt, which is insoluble in water, dissolves even in such feeble acids as acetic and sulphurous, and even in water containing carbonic acid. The latter fact is of immense importance in nature, since by reason of it rain water is able to transfer the calcium phosphates in the soil into solutions which are absorbed by plants. The solubility of the normal salt in acids takes place by virtue of the formation of an acid salt, which is evident from the quantity of acid required for its solution, and more especially from the fact that the acid solutions when evaporated give crystalline scales of the acid calcium phosphate, $CaH_4(PO_4)_2$, soluble in water. This solubility of the acid salt forms the basis of the treatment by acids of bones, phosphorites, guano, and other natural products containing the normal salt and employed for fertilising the soil. The

As a hydrate, orthophosphoric acid should be expressed, after the fashion of other hydrates, as containing three water residues (hydroxyl groups), i.e., as $PO(OH)_3$. This method of expression indicates that the type PX_5, seen in PH_4I, is here preserved, with the substitution of X_2 by oxygen and X_3 by three hydroxyl groups. The same type appears in $POCl_3$, PCl_5, PF_5, &c. And if we recognise phosphoric acid as $PO(OH)_3$, we should expect to find three anhydrides corresponding with it: (1) $[PO(OH)_2]_2O$, in which two of the three hydroxyls are preserved; this is pyrophosphoric acid, $H_4P_2O_7$. (2) $PO(OH)O$, where only one hydroxyl is preserved. This is metaphosphoric acid. (3) $(PO)_2O_3$ or P_2O_5, that is, perfect phosphoric anhydride. Therefore, **pyro- and meta-phosphoric acids are imperfect anhydrides** (or anhydro-acids) **of orthophosphoric acid.**[19]

Pyrophosphoric acid, $H_4P_2O_7$, is formed by heating orthophosphoric acid to 250°, when it loses water.[19a] Its normal salts are formed by igniting the dimetallic salts of orthophosphoric acid of the types HM_2PO_4. Thus from the disodium salt we obtain sodium pyrophosphate, $Na_4P_2O_7$ (it crystallises from water with $10H_2O$, is very

---

complete decomposition requires at least $2H_2SO_4$ to $Ca_3(PO_4)_2$, but in reality less is taken, so that only a portion of the normal salt is converted into the acid salt. Hydrochloric acid is sometimes used. (In practice such mixtures are known as **superphosphates.**) Certain experiments, however, show that a thorough grinding, the presence of organic, and especially of nitrogenous, substances, and the porous structure of some calcium phosphates (for example, in burnt bones), render the treatment of phosphoric manures by acids superfluous—that is, the crop is not improved by it.

[19] In this sense the ortho-acid itself might be considered as an anhydro-acid, regarding $P(HO)_5$ as the perfect hydrate, if PH_5 existed; but as, in general, the normal hydrates correspond with the existing hydrogen compounds with the addition of up to 4 atoms of oxygen, PH_3O_4 is the normal acid, just as SH_2O_4 and $ClHO_4$ are; while NHO_3, CH_2O_3 are meta-acids, or higher normal acids (NH_3O_4 and CH_4O_4) with the loss of a molecul of water.

In order to see the relation between the ortho-, pyro-, and meta-phosphoric acids, the first thing to remark in them is that the anhydride P_2O_5 is combined with 3, 2, and 1 molecules of water. In the absence of data for the molecular weight of ortho- and pyrophosphoric acids it is necessary to mention that all existing data for meta-phosphoric acid indicate (note 21) that its molecule is much more complex and contains at least $H_3P_3O_9$ or $H_6P_6O_{18}$. The explanation of the problems which here present themselves can, it seems to me, be only looked for after a detailed study of the phenomena of the polymerisation of mineral substances, and of those complex acids, such as phosphomolybdic, which we shall hereafter describe (Chap. XXI.). A similar instance is exhibited in the solubility of hydrate of silica (produced by the action of silicon fluoride on water) in fused metaphosphoric acid, with the formation, on cooling, of an octahedral compound (sp. gr. 3·1) of the composition SiO_2,P_2O_5. A certain indication (but no proof) that ordinary orthophosphoric acid is polymerised is given by Staudenmaier (1893), who obtained a salt, $K_5H_4P_3O_{12}$, by the action of a solution of KH_2PO_4 upon K_2CO_3, and a compound, $KH_3P_2O_8$, corresponding to the doubled molecule of H_3PO_4, by the action of KH_2PO_4 upon H_3PO_4 itself.

[19a] According to Watson (1893) the ortho-acid is partially transformed into the pyro-acid at 230 , whilst at 260° the latter begins to volatilise. At 300° the meta-acid only is formed.

stable, fuses when heated, and has an alkaline reaction ;[19b] and the monosodium salt, NaH_2PO_4, yields the acid salt, $Na_2H_2P_2O_7$ (easily soluble in water), which has an acid reaction, and when ignited further gives the meta-salt.[20]

Metaphosphoric acid, HPO_3 (the analogue of nitric acid), is formed by the ignition of the pyro- and ortho-acids (or, better, of their ammonium salts), as a vitreous, hygroscopic, fused mass (glacial phosphoric acid, *acidum phosphoricum glaciale*), soluble in water and volatilising without decomposition. It is also formed in the first slow action of cold water on the anhydride, but metaphosphoric acid gradually changes into the ortho-acid when its solution is boiled, or when it is kept for any length of time, especially in the presence of acids.[21]

[19b] Solutions of the pyro-acid gradually, but very slowly, pass into the ortho-acid if kept at the ordinary temperature; the first day about 5 per cent. of the acid is converted into ortho-acid, then the conversion proceeds still more slowly, so that after the course of three months only about half the acid is converted. The presence of acids and also heating facilitate the conversion. The neutral sodium salt is more stable than the acid, and its solutions do not change on (prolonged ?) boiling.

[20] The method of preparation of the acid itself consists in converting the sodium salt, $Na_4P_2O_7$, by double decomposition with water and a salt of lead, into insoluble lead pyrophosphate, $Pb_2P_2O_7$, which is then suspended in water and decomposed by sulphuretted hydrogen ; lead sulphide is thus precipitated, and pyrophosphoric acid remains in solution. The solution is evaporated under the receiver of an air-pump. It concentrates to a syrup and crystallises, and when ignited in this form loses water and forms metaphosphoric acid. It resembles orthophosphoric acid in many respects; its salts with the alkalies are also soluble, and the others insoluble in water but soluble in acids. When heated in solution with acid it gives orthophosphoric acid, as well as when fused with an excess of alkali.

Witt heated ammonium chloride with phosphoric acid (hydrochloric acid was evolved), ignited the residue to drive off ammonia, and obtained pyrophosphoric acid in the residue.

[21] As, when using phenolphthalein as an indicator in neutralising with an alkali, metaphosphoric acid is monobasic, and orthophosphoric acid dibasic, it is possible by means of this difference to follow the transition of meta- into ortho-phosphoric acid. Sabatier (1888) carried on an investigation of this nature, and found that the rate of transformation is dependent on the temperature, and is subject to the general laws of the rate of chemical transformations which belong to physical chemistry.

Metaphosphoric acid has a particular interest in respect to the variations to which its salts are subject. The metaphosphates are formed by the ignition of the acid orthophosphates, MH_2PO_4, or MNH_4HPO_4, or of the acid pyrophosphates, $M_2H_2P_2O_7$, or $M_2(NH_4)_2P_2O_7$, water and ammonia being given off in the process. The properties of the metaphosphates, which have a similar composition to nitrates—for instance, $NaPO_3$, or $Ba(PO_3)_2$—vary according to the duration of the ignition to which the ortho-, or pyrophosphates from which they are prepared have been subjected. When the salts NaH_2PO_4 or NH_4NaHPO_4 are strongly ignited, a salt, $NaPO_3$, is formed, which deliquesces in the air, and gives a gelatinous precipitate with salts of the alkaline earths. But, as Graham (in 1830–40), and many others, especially Fleitmann and Hanneberg (in 1840–50), and Tammann (in the nineties), observed, under other conditions the salts of the same composition acquire other properties. The above chemists recognise five polymeric forms of metaphosphates, $(HPO_3)_n$. We shall follow the nomenclature and researches of Fleitmann.

Monometaphosphoric acid. The salts are distinguished for their insolubility in

In order to see the relation between phosphoric acid and the lower acids of phosphorus, it is simplest to imagine the substitution of hydroxyl in H_3PO_4 or $PO(OH)_3$ by hydrogen. Then from orthophosphoric acid, $PO(OH)_3$ we shall obtain phosphorous acid, $POH(OH)_2$, and hypophosphoric acid, $POH(OH)$; and, furthermore, phosphorous acid should be dibasic if orthophosphoric acid is tribasic, and hypophosphorous acid should be monobasic. This conclusion[21a] is, in

---

water; even the salts $NaPO_3$, KPO_3, are insoluble. They are obtained by igniting the monometallic orthophosphates—for example, RH_2PO_4—up to the temperature at which all water is evolved (316°), but not to fusion. No double salts are known.

Dimetaphosphoric acid, on the contrary, easily forms double salts—for example, $KNaP_2O_6$, and also the copper potassium salt, &c. The copper salt is obtained by evaporating a solution of copper oxide in orthophosphoric acid. A blue ortho-salt, $CuRHO_4$, first separates from the solution, then a light-blue pyro-salt, $Cu_2P_2O_7$; and above 350°, when metaphosphoric acid itself begins to volatilise, the dimetaphosphate, CuP_2O_6, is formed. The residue is washed with water, and decomposed with a hot solution of sodium sulphide, when the sodium salt, $Na_2P_2O_6$, is obtained in solution. This salt, when evaporated with alcohol, gives crystals which contain 2 mols. of H_2O, but retain their solubility (in 7 parts of water) after the water is driven off at 100°. When fused, these crystals give a deliquescent salt (hexa-metaphosphate). The solution of the salt has a neutral reaction, which only after prolonged boiling becomes acid, owing to the formation of orthophosphate, NaH_2PO_4. The soluble salts of dimetaphosphoric acid give the insoluble silver salt, $Ag_2P_2O_6$, with silver nitrate, and a precipitate of $BaP_2O_6,2H_2O$ with barium chloride.

Trimetaphosphoric acid is obtained as the sodium salt, $Na_3P_3O_9$, when any other metaphosphate of sodium is fused and *slowly* cooled, then dissolved in a slight excess of warm water, and the resultant solution evaporated. The crystals contain 6 mols. H_2O, and dissolve in four parts of water. An acid reaction is only obtained, as with the preceding salt, after prolonged boiling with water. The acid is a true analogue of nitric acid, because *all its metallic salts are soluble.*

Hexametaphosphoric acid. Fleitmann so named the ordinary metaphosphoric acid (glacial) which attracts moisture. The deliquescent sodium salt is obtained like the trimetaphosphate, only by *rapid* cooling. It is also formed by fusing silver oxide with an excess of phosphoric acid. The sodium salt is soluble in water, and gives viscous, elastic precipitates with salts of Ba, Ca, and Mg. Lubert (1893) obtained salts of Ag, Pb, &c.

Jawein and Thillot (1889), who investigated the sodium salts of metaphosphoric acid by Raoult's method, came to the conclusion that the salts of di- and tri-metaphosphoric acid behave in such a manner that their molecule must be represented as non-polymerised, $NaPO_3$, whilst those of hexametaphosphoric acid behave as $(NaPO_3)_4$. At all events the series of salts which Fleitmann and Henneberg regard as monometaphosphates—i.e., as non-polymerised—are most probably the most polymerised, because they are insoluble.

According to Tammann's researches, vitreous metaphosphoric acid contains a mixture consisting chiefly of two varieties, differing in the solubility and degree of stability of their salts. The least stable corresponds to Fleitmann's hexa-acid, and gives three isomeric salts. Tammann came to the conclusion that there exist polymers also in the form of penta-, octo-, and deca-metaphosphoric acids. Without going into details upon this subject, I do not think it superfluous to point out that the degree of polymerisation and the number of polymeric forms cannot yet be considered as sufficiently explained.

[21a] The dibasity of H_3PO_3, established by Würtz, has been proved by many direct experiments (see, for instance, note 22), among which we may mention that Amat (1892)

fact, true, and hence all the acids of phosphorus may be referred to one common type, PX_5, whose representatives are PH_4I and Cl_5, $POCl_3P$, PCl_2F_3, &c.

Phosphorous acid, PH_3O_3, is generally obtained from phosphorus trichloride, PCl_3, by the action of water: $PCl_3+3H_2O=3HCl+PH_3O_3$. Both acids formed are soluble in water, but are easily separated, because hydrochloric acid is volatile whilst phosphorous acid volatilises with difficulty, and if a small amount of water is originally taken the hydrochloric acid nearly all passes off directly. Concentrated solutions of phosphorous acid give crystals of H_3PO_3, which fuse at 70°, attract moisture from the air, and deliquesce when ignited, giving phosphine and phosphoric acid,[22] and are converted into orthophosphoric acid by many oxidising agents. In its salts only two hydrogen atoms are replaced by metals (Würtz); the salts of the alkaline metals are soluble, and give precipitates with the salts of the majority of other metals.

---

took a mixture of the aqueous solutions of Na_2HPO_3 and NaHO and added absolute alcohol to it. Two layers were formed; the upper, alcoholic one, contained all the excess of NaHO, whilst the lower only contained the salt Na_2HPO_3, which was therefore unable to react with the excess of NaHO. Amat also obtained NaH_2PO_3 by saturating H_3PO_3 with soda until he obtained a neutral reaction with methyl-orange. The replacement of one atom of H by sodium here, as in phosphoric acid (note 16), gives more heat than the replacement of the second atom. For the third atom there is no formation of a salt, and therefore no evolution of heat. The monometallic salts—for example, NaH_2PO_3—or the ammonium salts, when heated to 160°, give, as Amat had previously shown, a salt of dibasic pyrophosphorous acid, $Na_2H_2P_2O_5$.

[22] Phosphorous acid, when subjected to the action of nascent hydrogen (zinc and sulphuric acid), evolves phosphine, and when boiled with an excess of alkali it yields hydrogen ($PH_3O_3+3KHO=PK_3O_4+2H_2O+H_2$); owing to its liability to oxidation, it is a reducing agent—for instance, it reduces cupric chloride to cuprous chloride, and precipitates silver from the nitrate and mercury from its salts.

These reactions are connected with the fact that in this acid one atom of hydrogen should be considered as in the same condition as in phosphoretted hydrogen, which is expressed by the formula $PHO(OH)_2$, if we represent it as PH_4X, with the substitution of two of the hydrogen atoms by oxygen and of HX by two of hydroxyl. The direct passage of phosphorous chloride into phosphorous acid would, however, indicate that all three atoms of hydrogen in it occur in the form of hydroxyl, because no difference is known between the three atoms of chlorine in PCl_3—they all react alike, as a rule. However, Menschutkin, by acting on alcohol, C_2H_5OH, with phosphorous chloride, obtained hydrochloric acid and a substance $P(C_2H_5O)Cl_2$, and from this by the action of bromine he obtained ethyl bromide, C_2H_5Br, and a compound $PBrOCl_2$, which proves, to a certain extent, the existence of a difference between the three atoms of hydrogen in PH_3O_3. If we turn our attention to the formation of phosphine by the ignition of phosphorous acid, we see that $4PH_3O_3$ only evolves 3H in the form of PH_3, and therefore the residue—that is, $3PH_3O_4$—will still contain one hydrogen of the same nature as in phosphine, because in $4PH_3O_3$ we shall recognise four such hydrogens as in phosphine. We arrive at the same conclusion by examining the decomposition of hypophosphorous acid, $2PH_3O_2=PH_3+PH_3O_4$. In the two molecules of the monobasic hypophosphorous acid taken, there are only two atoms of hydrogen replaceable by metals, whilst in the molecule of the resultant phosphoric acid there are three. Perhaps relations of this nature determine the relative stability of the di-metallic salts of orthophosphoric acid.

The monobasic **hypophosphorous acid**, PH_3O_2, gives salts PH_2O_2Na, $(PH_2O_2)_2Ba$, &c.; the two remaining atoms of hydrogen (which exist in the same form as in phosphine, PH_3) are not replaceable by metals, and this determines the property of these salts of evolving phosphoretted hydrogen when heated (especially with alkalies). In acting on substances liable to reduction it is this hydrogen which acts, and, for example, **reduces** gold and mercury from the solutions of their salts, or converts cupric into cuprous salts. In all these instances the hypophosphorous acid is converted into phosphoric acid. Under the action of zinc and sulphuric acid it gives phosphine, PH_3. Nevertheless, neither hypophosphorous acid nor its dry salts absorb oxygen from the air. The salts of hypophosphorous acid are more soluble than those of the preceding acids of phosphorus. Thus the sodium salt $PNaH_2O_2$ does not give a precipitate with barium chloride, and the salts of calcium, barium, and many other metals are soluble.[23] The hypophosphites are prepared by boiling an alkali with phosphorus as long as phosphoretted hydrogen is evolved. The acid itself is obtained from barium hypophosphite (prepared in the same manner by boiling phosphorus in baryta water), by decomposing its solution with sulphuric acid. By concentration of the solution of hypophosphorous acid (it must not be heated above 130°, at which temperature it decomposes), a syrup is formed which is able to crystallise. In the solid state hypophosphorous acid fuses at +17°, and has the properties of a clearly defined acid.

The types PX_3 and PX_5, which are evident for the hydrogen and oxygen compounds of phosphorus, are most clearly seen in its halogen compounds,[24] to the consideration of which we shall now proceed, fixing our attention more especially on the chlorine compounds, as being the most important from the historical, theoretical, and practical points of view.

---

[23] Calcium hypophosphite is used in medicine. According to Cavazzi, a mixture of sodium hypophosphite, NaH_2PO_2, and sodium nitrate explodes violently.

[24] Fluorine and bromine give PX_3 and PX_5, like chlorine. With respect to iodine, PI_5 is, in a chemical sense, a very unstable substance, and generally **phosphorus tri-iodide** only is formed (from yellow or red phosphorus and iodine in the requisite proportions. It is a red crystalline substance, fuses at 55°, is easily decomposed by water, forming phosphorous and hydriodic acids, and when heated, it evolves iodine vapours and forms **phosphorus di-iodide**, PI_2. This substance may be obtained in the same manner as the preceding by taking a smaller proportion of iodine (8 parts of iodine to 1 part of phosphorus, whilst the tri-iodide requires 12·3); it also forms red crystals, which melt at 110°. When decomposed by water it gives not only phosphorous and hydriodic acids, but also phosphine and a yellow substance (a lower oxide of phosphorus). In its composition, di-iodide of phosphorus corresponds with liquid phosphoretted hydrogen, PH_2, but probably its molecular weight is much higher: P_2I_4 or P_3I_6, &c. As the iodine compounds of phosphorus give hydriodic and phosphorous acids with water, and as both these substances are reducing agents in the presence of water (and hydrates), iodide of phosphorus also acts as a reducing agent.

Phosphorus burns in chlorine, forming phosphorous chloride, PCl_3, and with an excess of chlorine, phosphoric chloride, PCl_5. The oxychloride, $POCl_3$, as the simplest chloranhydride according to the type PX_5, and also phosphoric chloride, correspond with orthophosphoric acid, $PO(OH)_3$, while phosphorous chloride, PCl_3, corresponds with phosphorous acid and the type PX_3. **Phosphorus oxychloride,** $POCl_3$, is a colourless liquid, boiling at 110°. Phosphorus trichloride is also a colourless liquid, boiling at 76°,[25] whilst phosphoric chloride

---

[25] In a liquid state the density of phosphorous chloride at 10° is 1·597, and therefore its molecular volume $= 137{\cdot}5/1{\cdot}597 = 86{\cdot}0$, and that of phosphorus oxychloride is equal to $153{\cdot}5/1{\cdot}693 = 90{\cdot}7$; hence the addition of oxygen has produced considerable increase in volume, just as in the conversion of sulphur dichloride, SCl_2, into sulphuryl chloride, $SOCl_2$, the volume changes from 64 to 71. It is the same with the boiling-points; phosphorus trichloride boils at 70°, the oxychloride at 100°, sulphur dichloride at 64°, and sulphuryl chloride at 78°—that is, the addition of oxygen raises the boiling-points.

The vapour densities of phosphorus trichloride and oxychloride correspond with their formulæ (Cahours, Würtz), being equal to half the molecular weight referred to hydrogen. But it is not so with phosphorus pentachloride. Cahours showed that the vapour density of phosphorus pentachloride referred to air is 3·65, or to hydrogen, 52·6, whilst according to the formula PCl_5, it should be 104·2. Hence this formula corresponds with four, and not with two, molecules. This shows that the vapour of phosphoric chloride contains two molecules and not one, so that in a state of vapour it splits up, like sal-ammoniac, sulphuric acid, &c. The products of disruption must here be phosphorous chloride, PCl_3, and chlorine, Cl_2, bodies which easily re-form phosphoric chloride, PCl_5, at a lower temperature. This decomposition of phosphoric chloride in its conversion into vapour is confirmed by the fact that the vapour of this almost colourless substance shows the greenish-yellow colour peculiar to chlorine. This dissociation of phosphoric chloride has been considered by some chemists as a sign that phosphorus, like nitrogen, does not give volatile compounds of the type PX_5, and that such substances are only obtained as unstable molecular compounds which break up when distilled; for example, PH_3,HI; PCl_3,Cl_2; NH_3,HCl; &c. To prove that the molecule PCl_5 actually exists, Würtz in 1870 showed that when mixed with the vapour of phosphorous chloride the vapour of phosphoric chloride is (from 160° to 190°) perfectly colourless, and has a density which is really near to that required by the formula—namely, to 104—and the same density was determined for the pentachoride in an atmosphere of chlorine. Hence, at low temperatures and in admixture with one of the products of dissociation, there is no longer that decomposition which occurs at higher temperatures—that is, we have here a case of dissociation proceeding at moderate temperatures.

An important proof in favour of the type PX_5 is exhibited by **phosphorus pentafluoride,** PF_5, obtained by Thorpe as a colourless gas which only corrodes glass after the lapse of time; it may be kept over mercury, and has a normal density. It is formed when liquid arsenic trifluoride, AsF_3, is added to phosphoric chloride surrounded by a freezing mixture: $3PCl_5 + 5AsF_3 = 3PF_5 + 5AsCl_3$.

In general, fluorine and phosphorus give stable compounds: PF_3, POF_3, and PF_5, as would be expected from the fact that in passing from Cl to I (i.e., as the atomic weight of the halogen increases) the stability of the compounds with P and the tendency to give PX_5 (note 24) decrease. **Phosphorus trifluoride** is obtained by heating a mixture of ZnF_2 and PBr_3, by the action of AsF_3 upon PCl_3, by heating phosphide of copper with PbF_2, &c. It is a strong-smelling gas, which liquefies at $-10°$ under a pressure of 40 atmospheres, giving a colourless liquid. It dissolves easily in (is absorbed by, reacts with) water, and acts upon glass; when mixed with Cl_2 it combines with it (Poulenc, 1891), forming PCl_2F_3, a colourless gas of normal density, which is transformed into a liquid at 8°, decomposes into $PF_3 + Cl_2$ at 250°, and, with a small amount is a solid yellowish substance, which volatilises without melting at about 168°. They are all heavier than water, and form types of the **chloranhydrides** or chlorine compounds of the non-metallic elements whose hydroxides are acids, just as NaCl and $BaCl_2$ are types of halogen metallic salts.

If a piece of phosphorus is dropped into a flask containing chlorine, it burns when touched with a red-hot wire, and combines with the chlorine. If the phosphorus is in excess, liquid **phosphorus trichloride**, PCl_3, is always formed, but if the chlorine is in excess the solid pentachloride is obtained. The trichloride is prepared in the following manner. Dry chlorine (passed through a series of Woulfe's bottles containing sulphuric acid) is led into a retort containing sand and phosphorus. The retort is heated, the phosphorus melts, spreads through the sand, and gradually forms the trichloride, which distils over into a receiver, where it condenses. **Phosphoric chloride** or **phosphorus pentachloride**, PCl_5, is prepared by passing dry chlorine into a vessel containing phosphorus trichloride (purified by distillation). Phosphorous chloride combines directly with oxygen, but more rapidly with ozone or with the oxygen of potassium chlorate ($3PCl_3 + KClO_3 = 3POCl_3 + KCl$), forming **phosphorus oxychloride**, $POCl_3$ (Brodie). This compound is also formed by the first action of water on phosphoric chloride; for example, if two vessels, one containing phosphoric chloride and the other water, are placed under a bell-jar, after a certain time the crystals of the chloride disappear and hydrochloric acid passes into the water. The aqueous vapour acts on the pentachloride: $PCl_5 + H_2O = POCl_3 + 2HCl$, the result being that liquid phosphorus oxychloride is found in one vessel and a solution of hydrochloric acid in the other. However, an excess of water directly transforms phosphoric chloride into orthophosphoric acid, $PCl_5 + 4H_2O = PH_3O_4 + 5HCl$,[26] since $POCl_3$ reacts with water ($3H_2O$), forming 3HCl and phosphoric acid, $PO(OH)_3$.

---

of water, gives **oxy-fluoride of phosphorus**, POF_3 (with a large amount of water it gives PH_3O_4), which Moissan (1891) obtained by the action of dry HF upon P_2O_5, and Thorpe and Tutton (1890) by heating a mixture of cryolite and P_2O_5. It is a gas of normal density, like PF_3, and was obtained by Moissan by the action of fluorine upon PF_3. Thus, the forms PX_3 and PX_5 not only exist in many solid and non-volatile substances, but also as vapours (PSF_3; see Chap. XX., note 20).

[26] Phosphorus oxychloride is obtained by the action of phosphoric chloride on hydrates of acids (because alkalies decompose phosphorus oxychloride), according to the equation, $PCl_5 + RHO = POCl_3 + RCl + HCl$, where RHO is an acid. The reaction only proceeds according to this equation with monobasic acids, but then RCl is volatile, and therefore a mixture is obtained of two volatile substances, the acid chloride and phosphorus oxychloride, which are sometimes difficult to separate; whilst if the hydrate be polybasic, the reaction frequently proceeds so that an anhydride is formed: $RH_2O_2 + PCl_5 = RO + POCl_3 + 2HCl$. If the anhydride be non-volatile (like boric), or

The above chlorine compounds serve not only as a type of the chloranhydrides, but also as a means for the preparation of other **acid chloranhydrides.** Thus the conversion of acids XHO into chloranhydrides, XCl, is generally accomplished by means of phosphorus pentachloride. This fact was discovered by Chancel, and adopted by Gerhardt as an important method for studying organic acids. By this means organic acids, containing, as we know, RCOOH (where R is a hydrocarbon group, and where carboxyl may repeat itself several times by replacing the hydrogen of hydrocarbon compounds), are converted into their chloranhydrides, RCOCl. With water they again form the acid, and resemble the chloranhydrides of mineral acids in their general properties.

Since carbonic acid, $CO(OH)_2$, contains two hydroxyl groups, its perfect chloranhydride, $COCl_2$, **carbonic oxychloride, carbonyl chloride** or **phosgene gas**, contains two atoms of chlorine, and differs from the chloranhydrides of organic acids in that in them one atom of chlorine is replaced by the hydrocarbon radicle, RCOCl, if R be a monatomic radicle giving a hydrocarbon RH. It is evident, on the one hand, that in RCOCl the hydrogen is replaced by the radicle COCl, which is also able to replace several atoms of hydrogen (for example, $C_2H_4(COCl)_2$ corresponds with the bibasic succinic acid); and, on the other hand, that the reactions of the chloranhydrides of organic acids will answer to the reactions of carbonyl chloride, as the reactions of the acids themselves answer to those of carbonic acid. Carbonyl chloride is obtained directly from dry carbon monoxide and chlorine[27]

---

easily decomposed (like oxalic), it is easy to obtain pure oxychloride. Thus, phosphorus oxychloride is often prepared by acting on boric or oxalic acid with phosphoric chloride. It is also formed when the vapour of phosphoric chloride is passed over phosphoric anhydride, $P_2O_5 + 3PCl_5 = 5POCl_3$. This forms an excellent example in proof of the fact that the formation of one substance from two does not necessarily show that the resultant compound contains the molecules of these substances in its molecule. But other oxychlorides of phosphorus are also formed by the interaction of phosphoric anhydride and chloride; thus at 200°, PO_2Cl, or chloranhydride of metaphosphoric acid, is formed (Gustavson). The chloranhydride of pyrophosphoric acid, $P_2O_3Cl_4$, was obtained (Hayter and Michaelis), together with NOCl, &c., by the action of NO upon cold PCl_3, as a fuming liquid boiling at 210°.

[27] The direct action of the sun's rays, or of magnesium light, is necessary to start the reaction between carbonic oxide and chlorine, but when once started it will proceed rapidly in diffused light. An excess of chlorine (which gives its coloration to the colourless phosgene) aids the completion of the reaction, and may afterwards be removed by metallic antimony. Porous substances, like charcoal, aid the reaction. Phosgene may be prepared by passing a mixture of carbonic anhydride and chlorine over incandescent charcoal. Lead chloride or silver chloride, when heated in a current of carbonic oxide, also partially forms phosgene gas. Carbon tetrachloride, CCl_4, also forms it when heated with carbonic anhydride (at 400°), with phosphoric anhydride (200°), and most easily of all with sulphuric anhydride ($2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2$, this is pyrosulphuryl chloride). Chloroform, $CHCl_3$, is converted into carbonyl chloride when heated

exposed to the action of light, and forms a colourless gas, which easily condenses into a liquid, boiling at +8°, specific gravity 1·43, and having the suffocating odour belonging to all chloranhydrides. Like all chloranhydrides, it is immediately decomposed by water, forming carbonic anhydride, according to the equation, $COCl_2 + H_2O = CO_2 + 2HCl$, and thus expresses the type proper to all chloranhydrides of both mineral and organic acids.[28]

In order to show the general method for the preparation of acid chloranhydrides, we will take that of acetic acid, $CH_3{\cdot}COOH$, as an example. Phosphorus pentachloride is placed in a glass retort, and acetic acid poured over it; hydrochloric acid is then evolved, and the substance distilling over directly after is a very volatile liquid, boiling at 50°, and having all the properties of the chloranhydrides. With water it forms hydrochloric and acetic acids. The resultant oxychloride boils at 110°, and may therefore be easily separated. The general scheme for the reaction of phosphorus pentachloride with hydrates ROH is exactly the same as with water; namely, ROH with PCl_5 gives $POCl_3 + HCl + RCl$—that is, a chloranhydride, in this case CH_3COCl.[28a]

---

with $SO_2(OH)Cl$ (the first chloranhydride of sulphuric acid); $CHCl_3 + SO_3HCl = COCl_2 + SO_2 + 2HCl$ (Dewar), and when oxidised by chromic acid. Among the reactions of phosgene we may mention the formation of urea with ammonia, and of carbonic oxide when heated with metals.

[28] We are already acquainted with some of the chloranhydrides of the inorganic acids—for instance, BCl_3 and $SiCl_4$—and we shall describe those which correspond with sulphuric acid in the following chapter. It may be mentioned here that, when hydrochloric acts on nitric acid (Aqua Regia, Chap. XI.), there is formed, besides chlorine, the oxychlorides $NOCl$ and NO_2Cl, which may be regarded as **chloranhydrides of nitric and nitrous acids**. The former boils at −5°, the latter at +5°; the specific gravity of the first at −12° is 1·416, and at −18°, 1·433 (Geuther), and that of the second, 1·3; the first is obtained from nitric oxide and chlorine, the second from nitric peroxide and chlorine, and also by the action of phosphoric chloride on nitric acid. If the gases evolved by aqua regia are passed into cold strong sulphuric acid, they form crystals of the composition $NHSO_3$ (like chamber crystals), which melt at 86°, and with sodium chloride form acid sodium sulphate and the oxychloride $NOCl$. This chloranhydride of nitric acid is termed **nitrosyl chloride**.

Cyanogen chloride, $CNCl$, is the gaseous chloranhydride of cyanic acid; it is formed by the action of chlorine on aqueous mercury cyanide, $Hg(CN)_2 + 2Cl_2 = HgCl_2 + 2CNCl$. When chlorine acts on cyanic acid, it forms not only this cyanogen chloride, but also polymerides of it—a liquid, boiling at 18°, and a solid, boiling at 190°. The latter corresponds with cyanuric acid, and consequently has the composition $C_3N_3Cl_3$. Details concerning these substances must be looked for in works on organic chemistry.

[28a] This reaction, indeed, proceeds very easily and completely with a number of hydroxides, if they do not react on hydrochloric acid and phosphorus oxychloride, which is the case when they have alkaline properties. When the hydroxide is dibasic and is present in excess, it not infrequently happens that the elements of water are taken up: $R(OH)_2 + PCl_5 = RO + 2HCl + POCl_3$. The anhydride RO may then be converted into chloranhydride, $RO + PCl_5 = RCl_2 + POCl_3$.

Phosphorus trichloride and oxychloride act in a similar manner to phosphoric chloride. When phosphorus trichloride acts on an acid, $3RHO + PCl_3 = 3RCl + P(HO)_3$. If a salt

Containing, as they do, chlorine, which easily reacts with hydrogen, phosphorus pentachloride, trichloride, and oxychloride enter into reaction with ammonia, and give a series of amide and nitrile compounds of phosphorus. Among these a **mono-amido-orthophosphoric acid,** $PO(NH_2)(OH)_2$ was obtained by Stokes by saponifying the phenol ether, $PO(NH_2)(OC_6H_5)_2$, formed from $POCl_3$ and C_6H_5OH after treating the resultant $POCl(OC_6H_5)_2$ with ammonia. An alkaline salt is produced by the saponification and is first converted into a lead salt, and then into the amido-orthophosphoric acid. It is soluble in water but not in alcohol, and forms, as would be expected, both acid and neutral salts, i.e., mono- and di-metallic, but the former give a neutral reaction with litmus, as would be expected from the example of orthophosphoric acid itself. Schiffer, by acting on $POCl_3$ with ammonia, obtained sal-ammoniac (which is afterwards removed by water) and an orthophosphoric triamide, $PO(NH_2)_3$, as a white insoluble powder on which dilute acids and alkalies do not act, but which, when fused with potassium hydroxide, gives potassium phosphate and ammonia like other amides. When ignited, the resultant triamide (its preparation under these conditions has been repeatedly denied) liberates ammonia and forms the nitrile PON, just as urea, $CO(NH_2)_2$, gives off ammonia and forms the nitrile CONH. This nitrile, sometimes called **monophosphamide,** although it is undoubtedly the **nitrile** of metaphosphoric acid, corresponds with metaphosphoric acid, namely, with its ammonium salt: $NH_4PO_3-2H_2O=PON$. This relation is confirmed by the fact that PON, moistened with water, gives metaphosphoric acid when ignited and K_3PO_4 when fused with KHO. It is the analogue of nitrous oxide, NON. It is a very stable compound, colourless, and probably a polymeride.[29]

---

is taken, then by the action of phosphorus oxychloride a corresponding chloranhydride and salt of orthophosphoric acid are easily formed: $3R(KO)+POCl_3=3RCl+PO(KO)_3$. The chloranhydride RCl is always more volatile than its corresponding acid, and distils over before the hydrate RHO. Thus acetic acid boils at 117°, and its chloranhydride at 50°. A chloranhydride RCl is frequently employed for the formation of other compounds of a given radicle R; for instance, with ammonia they form amides RNH_2, and with salts ROK, with anhydrides R_2O, &c.

[29] The reaction of ammonia on phosphorus pentachloride is more complex than the preceding. This is readily understood: to the oxychloride, $POCl_3$, there corresponds a hydrate $PO(OH)_3$, and a salt $PO(NH_4O)_3$, and consequently also an amide $PO(NH_2)_3$, whilst the pentachloride, PCl_5, has no corresponding hydrate $P(OH)_5$, and therefore there is no amide $P(NH_2)_5$. The reaction with ammonia will be of two kinds: either instead of 5 mols. of NH_3, only 3 mols. or still less will act, i.e., $PCl_2(NH_2)_3$, $PCl_3(NH_2)_2$, &c., are formed; or else the pentachloride will act like a mixture of chlorine with the trichloride, and then as the result there will be obtained the products of the action of chlorine on those amides which are formed from phosphorus trichloride and ammonia. It would appear that both kinds of reaction proceed simultaneously, but both kinds of products are unstable, at all events complex, and in the result there is obtained a mixture containing

The nearest analogue of phosphorus is **arsenic**, the metallic aspect of which and, what is far more important, the general character of

sal-ammoniac, &c. The products of the first kind should react with water, and we should obtain, for example, $PCl_3(NH_2)_2 + 2H_2O = 3HCl$ and $PO(HO)(NH_2)_2$. This substance has actually been obtained in a crystalline form, and the compound $PONH(NH_2)$ derived from it by elimination of the elements of water is known, and is termed **diphosphamide**: it is, however, more probable that it is a nitrile than an amide, because only amides contain the group NH_2. It is a colourless, stable, insoluble powder, which possibly corresponds with pyrophosphoric acid, more especially since, when heated, it evolves ammonia and gives phosphoryl nitride, PON—that is, the nitrile of metaphosphoric acid. The amide corresponding with the pyrophosphate, $P_2O_3(NH_4O)_4$, should be $P_2O_3(NH_2)_4$, and the nitriles corresponding to the latter would be $P_2O_2N(NH_2)_3$, $P_2ON_2(NH_2)_2$, and $P_2N_3(NH_2)$. The composition of the first is the same as that of the above diphosphamide. The third pyrophosphoric nitrile has a formula $P_2N_4H_2$, and this is the composition of the body known as **phospham**, PHN_2 (in a certain sense this is the analogue of N_3H polymerised, Chap. VI.). Indeed, phospham has been obtained by heating the products of the action of ammonia on phosphoric chloride, as an insoluble and alkaline powder, which gives ammonia and phosphoric acid when subjected to the action of water. The same substance is obtained by the action of ammonium chloride on phosphoric chloride ($PNCl_2$ is first formed, and reacts further with ammonia, forming phospham), and by igniting the mass which is formed by the action of ammonia on phosphorus trichloride. Formerly the composition of phospham was supposed to be PN_2, but now there is reason to think that its molecular formula is $P_3H_3N_6$.

The above compounds correspond with normal salts, but nitriles and amides corresponding to acid salts are also possible, and they will be acids. For example, the amide $PO(HO)_2(NH_2)$, and its nitrile, will be either $PN(HO)_2$ or $PO(HO)(NH)$, but at all events of the composition PNH_2O_2, and having acid properties. The ammonium salt of this **phosphonitrilic acid** (it is called phosphamic acid), $PNH(NH_4)O_2$, is obtained by the action of ammonia on phosphoric anhydride, $P_2O_5 + 4NH_3 = H_2O + 2PNH(NH_4)O_2$. A non-crystalline soluble mass is thus formed, which is dissolved in a dilute solution of ammonia and precipitated with barium chloride, and the resultant barium salt is then decomposed with sulphuric acid, and thus a solution of the acid of the above composition is obtained.

It is evident from the theory of the formation of amides and nitriles (Chap. IX.) that very many compounds of this kind can correspond with the acids of phosphorus; but as yet only a few are known. The easy transitions of the ortho-, meta-, and pyro-phosphoric acids, by means of the hydrogen of ammonia, into the lower acids, and conversely, tend to complicate the study of this very large class of compounds, and it is rarely that the nature of a product thus obtained can be judged from its composition; and this is all the more so since instances of isomerism and polymerism, &c., are here possible. Many data are yet needed to enable us to form a true judgment as to the composition and structure of such compounds, although this subject was much studied by Liebig, Gerhardt, Gladstone, and others in former days, and more recently Thorpe, Mente, Stokes, and others have supplemented and corrected the former data. As an instance of the difficulties encountered we will describe the very interesting and most fully investigated compound of this class, $PNCl_2$, called **chlorophosphamide**, or nitrogen chlorophosphorite. It is formed in small quantities when the vapour of phosphoric chloride is passed over ignited sal-ammoniac. Besson (1892) heated the compound $PCl_5,8NH_3$ (which is easily and directly formed from PCl_5 and NH_3) under a pressure of about 50 mm. (of mercury) to 200°, and obtained brilliant crystals of $PNCl_2$, which melted at 106° (in the residue after the distillation of sal-ammoniacal phospham). The chlorine in it is very stable—quite different from that in phosphoric chloride. Indeed, the resultant substance is not only insoluble in water (though soluble in alcohol and ether), but it is not even moistened by it, and distils over, together with steam, without being decomposed. In a free state it readily crystallises in colourless prisms, fuses at 114°, boils at 250°, and when fused with potash gives potassium whose compounds, AsX_3 and AsX_5, at once recall the metals. The hydrate of its highest oxide, arsenic acid (ortho-arsenic acid), H_3AsO_4, is an oxidising agent, like the acids of the metals and easily gives up a portion of its oxygen to many other substances; but, nevertheless, it is very like phosphoric acid. Mitscherlich established the conception of isomorphism by comparing the salts of these acids.[30]

Arsenic occurs **in nature**, not only combined with metals, but also, although rarely, native and also in combination with sulphur in two minerals—one red, *realgar*, As_2S_2, and the other yellow, *orpiment*, As_2S_3 (Chap. XX., note 29). Arsenic occurs, but more rarely, in the form of salts of arsenic acid—for instance, the so-called cobalt and nickel blooms, two minerals which are found accompanying other cobalt ores, are the arsenates of these metals. Arsenic is also found in certain clays (ochres) and has been discovered in small quantities in some mineral springs, but it is in general of rarer occurrence in nature than phosphorus. Arsenic is most frequently extracted from arsenical pyrites, FeSAs, which, when roasted without access of air, evolves the vapour of arsenic, ferrous sulphide being left behind. It is also obtained by heating arsenious anhydride with charcoal, in which case carbonic oxide is evolved. In general, the oxides and other compounds are very easily reduced. Solid **arsenic** is a steel-grey brittle **metal**, having a bright lustre and scaly structure. Its specific gravity is 5·7. It is opaque and infusible, but volatilises without fusion (in a sealed vessel it fuses at about 480°) as a colourless or slightly yellow vapour, which, on cooling, deposits rhombohedral crystals.[30a] The vapour

---

chloride and the amidonitrile of phosphoric acid. Judging from its formula and the simplicity of its composition and reactions, it might be thought that the molecular weight of this substance would be expressed by the formula PCl_2N, that it corresponds with PON and with PCl_5 (like $POCl_3$), with the substitution of Cl_3 by N, just as in $POCl_3$ two atoms of chlorine are replaced by oxygen; but all these surmises are incorrect, because its vapour density (referred to hydrogen—Gladstone, Wichelhaus) is 182—that is, the molecular formula must be three times greater, $P_3N_3Cl_6$. The polymerisation (tripling) is here of exactly the same kind as with the nitriles, metaphosphoric acid, and many other compounds of phosphorus.

[30] It is necessary to remark that, although arsenic is so closely analogous to phosphorus (especially in the higher forms of combination, RX_3 and RX_5), at the same time it exhibits a certain resemblance and even isomorphism with the corresponding compounds of sulphur (especially the lower metallic compounds of the type MAs, which correspond with MS). Thus compounds containing metals, arsenic, and sulphur are very frequently met with in nature. Sometimes the relative amounts of arsenic and sulphur vary, so that an isomorphous substitution between the arsenides and sulphides must be recognised. Besides FeS_2 (ordinary pyrites), and $FeAs_2$, iron forms an arsenical pyrites containing sulphur and arsenic, which from its composition, FeAsS or FeS_2FeAs_2, resembles the two preceding.

[30a] According to Retgers (1893) the arsenic mirror (see further on) is an unstable variety of metallic arsenic, whilst the brown product which is formed together with it in Marsh's apparatus is a lower hydride, AsH. Schuller and McLeod (1894), however,

density of arsenic is 150 times greater than that of hydrogen—that is, its molecule, like that of phosphorus, contains 4 atoms, As_4. The vapour density decreases at about 1,700°, and corresponds to As_2 (V. Meyer, 1889). When heated in the air, arsenic easily oxidises into white arsenious anhydride, As_2O_3, but even at the ordinary temperature it loses its lustre (becomes dull), owing to the formation of a coating of a lower oxide. The latter appears to be as volatile as arsenious anhydride, and it is probable that it is owing to the presence of this compound that the vapours of arsenious compounds, when heated with charcoal (for example, in the reducing flame of a blowpipe), have the characteristic smell of garlic, because the vapour of arsenic itself apparently has not this odour.

Arsenic easily combines with bromine and chlorine,[31] while nitric

---

consider it to be a peculiar **yellow variety of arsenic.** This latter view is now generally accepted, because yellow arsenic in a solid form *soon passes into the ordinary metallic and opaque variety under the influence of the sun's rays* (but as far as I know it has not yet been shown whether hydrogen is evolved or not in this change), and this, together with its solubility in bisulphide of carbon, CS_2, forms the chief characteristic of this substance (Erdmann and Unruh, 1901). It is obtained by heating metallic arsenic to volatilisation in a current of dry CO_2, and rapidly cooling the resultant vapour in a stream of refrigerated CO_2, and leading the mixture of arsenic vapour and CO_2 into vessels containing CS_2 which are kept in the dark and at a low temperature. The solution in CS_2 thus obtained deposits yellow crystals on evaporation. According to Prof. Erdmann the rise in the boiling-point of the CS_2 indicates that the molecule of arsenic has the composition As_4, just as in a state of vapour. This variety of arsenic evidently corresponds to ordinary yellow phosphorus, P_4, but is more unstable.

[31] Hydrochloric acid dissolves arsenious anhydride in considerable quantities, and this is probably owing to the formation of unstable compounds in which the arsenious anhydride plays the part of a base. A compound called **arsenious oxychloride**, having the composition AsOCl, is even known. It is formed when arsenious anhydride is added little by little to boiling arsenic trichloride, $As_2O_3 + AsCl_3 = 3AsOCl$. It is a transparent substance, which fumes in air, and combines with water to form a crystalline mass having the composition $As(OH)_2Cl$. When heated it decomposes into arsenious chloride and a fresh oxychloride of a more complex composition, $As_6O_8Cl_2$. Arsenic trichloride, when treated with a small quantity of water, forms the crystalline compound, $As(OH)_2Cl$, mentioned above. These compounds resemble the basic salts of bismuth and aluminium. The existence of these compounds shows that arsenic is of a more metallic or basic character than phosphorus. Nevertheless **arsenic trichloride,** $AsCl_3$, resembles phosphorus trichloride in many respects. It is obtained by the direct action of chlorine on arsenic, or by distilling a mixture of common salt, sulphuric acid, and arsenious anhydride. Arsenious chloride is a colourless oily liquid, boiling at 134°, and having a sp. gr. of 2·20. It fumes in air like other chloranhydrides, but is much more slowly and imperfectly decomposed by water than phosphorus trichloride. A considerable quantity of water is required for its complete decomposition into hydrochloric acid and arsenious anhydride. It forms an excellent example of the transition from true metallic chlorides to true chloranhydrides of the acids. It hardly combines with chlorine, i.e., if $AsCl_5$ is formed it is very unstable. **Arsenic tribromide,** $AsBr_3$, is formed as a crystalline substance, fusing at 31° (Walden, 1902), and boiling at 221°, by the direct action of metallic arsenic on a solution of bromine in carbon bisulphide, the latter being then evaporated. The specific gravity of arsenic tribromide is 3·36. Crystalline arsenic tri-iodide, AsI_3, having a sp. gr. 4·39, may be obtained in a like manner; it may be dissolved in water,

acid and aqua regia oxidise it into the higher oxide, or rather its hydrate, arsenic acid.[32] As far as is known, it does not decompose steam, and acts exceedingly slowly on those acids, like hydrochloric, which are not capable of oxidising. It is employed in certain alloys—for instance, 1 to ½ per cent. of arsenic is added to lead for making bullets in order to render it more fusible.

Arseniuretted hydrogen, arsine, AsH_3, resembles phosphoretted hydrogen in many respects. This colourless gas, which liquefies into a mobile liquid at about −50°, and solidifies at about −110°, has a disagreeable garlic-like odour, is only slightly soluble in water, and is exceedingly poisonous. Even in small quantity it causes great suffering, and if present to any considerable amount in air it even causes death. The other compounds of arsenic are also poisonous,

---

and on evaporation separates out from the solution in an anhydrous state—that is, it is not decomposed—and consequently behaves like metallic salts. **Arsenic trifluoride,** AsF_3, is obtained by heating fluor spar and arsenious anhydride with sulphuric acid. It is a fuming, colourless, and very poisonous liquid, which boils at 63° and has a sp. gr. of 2·73. It is decomposed by water. It is very remarkable that fluorine forms a pentafluoride of arsenic also, although this compound has not yet been obtained in a separate state, but only in combination with potassium fluoride. This compound, K_3AsF_8, is formed as prismatic crystals when potassium arsenate, K_3AsO_4, is dissolved in hydrofluoric acid.

[32] **Arsenic acid,** H_3AsO_4, corresponding with orthophosphoric acid, is formed by oxidising arsenious anhydride with nitric acid, and evaporating the resultant solution until it attains a sp. gr. of 2·2; on cooling it separates in crystals having the above composition. This hydrate corresponds with the normal salts of arsenic acid; but on dissolving in water (without heating), and on cooling a strong solution, crystals containing a greater amount of water, namely, $(AsH_3O_4)_2,H_2O$, separate. This water is easily expelled at 100°. At 120° crystals having a composition analogous with that of pyrophosphoric acid, $As_2H_4O_7$, separate, but water, on dissolving this hydrate with the development of heat, forms a solution in no way differing from a solution of ordinary arsenic acid, so that it is not an independent pyroarsenic acid that is formed. Neither is there any true analogue of metaphosphoric acid, but an intermediate hydrate of the composition $2As_2O_5,3H_2O$ is easily formed (Auger). Arsenic acid forms three series of salts, which are analogous with the three series of orthophosphates. Thus the normal salt, K_3AsO_4, is formed by fusing the other potassium arsenates with potassium carbonate; it is soluble in water and crystallises in needles which do not contain water. Di-potassium arsenate, K_2HAsO_4, is formed in solution by mixing potassium carbonate and arsenic acid until carbonic anhydride ceases to be evolved; it does not crystallise, and has an alkaline reaction; hence it corresponds perfectly with the sodium phosphate. As was mentioned above, arsenic acid itself acts as an oxidising agent; for example, it is used in the manufacture of aniline dyes for oxidising the aniline, and is prepared in large quantities for this purpose. When sulphuretted hydrogen is passed through its solution, sulphuric acid and arsenious anhydride are obtained in solution. When boiled with hydrochloric acid it evolves chlorine, like selenic, chromic, manganic, and certain other higher metallic acids.

Arsenic anhydride, As_2O_5, is produced from arsenic acid at 180°. It must be carefully heated, as it decomposes into oxygen and As_2O_3. Arsenic anhydride is an amorphous substance of sp. gr. 4·3 and almost insoluble in water, but it attracts moisture from the air, deliquesces, and passes into the acid. Hot water produces this transformation with great ease.

with the exception of the insoluble sulphur compounds.[32a] Arseniuretted hydrogen, AsH_3, is obtained by the action of water on the alloy of arsenic and sodium, sodium hydroxide and arseniuretted hydrogen being formed. It is also formed by the action of sulphuric acid on the alloy of arsenic and zinc: $Zn_3As_2+3H_2SO_4=2AsH_3+3ZnSO_4$.[33] The oxygen compounds of arsenic are very easily reduced by the action of hydrogen at the moment of its evolution from acids, and the reduced arsenic then combines with the hydrogen; hence, if a certain amount of an oxygen compound of arsenic be put into an apparatus containing zinc and sulphuric acid (and thus serving for the evolution of hydrogen), the hydrogen evolved will contain arseniuretted hydrogen. In this case it is diluted with a considerable amount of hydrogen. But its presence in the most minute quantities may be easily recognised from the fact that it is **easily decomposed** by heat (at 200° according to Brunn) into metallic arsenic and hydrogen, and therefore, if such impure hydrogen be passed through a moderately heated tube, metallic arsenic will be deposited as a bright layer on the part of the tube which was heated (see note 30a). This reaction is so sensitive that it enables the most minute traces of arsenic to be discovered; hence it is employed in medical jurisprudence as a test in poisoning cases. It is easy to

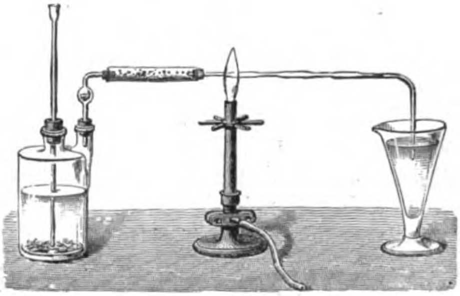


FIG. 95.—Formation and decomposition of arseniuretted hydrogen. Hydrogen is evolved in the Woulfe's bottle, and when the gas comes off, a solution containing arsenic is poured through the funnel. The presence of AsH_3 is recognised from the deposition of a mirror of arsenic when the gas-conducting tube is heated. If the escaping hydrogen be lighted, and a porcelain dish be held in the flame, a film of arsenic will be deposited on it. The gas is dried by passing through the tube containing calcium chloride. This apparatus is used for the detection of arsenic by Marsh's test.

[32a] A. P. Borodin showed that arsenic acid (so long as it is not deoxidised) is far less poisonous than arsenious acid. A. Gauthier proposed (1902) and essayed the action of the methyl-sodium salt, $As(CH_3)HNaO_4$, known as 'arenal,' as a drug for decreasing fever, as the least poisonous of the soluble preparations of arsenic, many of which are employed in small quantities in medicine.

[33] The formation of arseniuretted hydrogen is accompanied by the absorption of 37,000 heat units, while phosphine evolves 18,000 (Ogier), and ammonia 27,000. Sodium (0·6 per cent.) amalgam, with a strong solution of As_2O_3, gives a gas containing 86 vols. of arsenic and 14 vols. of hydrogen (Cavazzi).

discover the presence of arsenic in common zinc, copper, sulphuric and hydrochloric acids, &c., by this method. It is obvious that in testing for poison by Marsh's apparatus it is necessary to take zinc and sulphuric acid quite free from arsenic. The arsenic deposited in the tube may be driven as a volatile metal from one place to another in the current of hydrogen evolved, owing to its volatility. This forms a distinction between arseniuretted and antimoniuretted hydrogen, which is decomposed by heat in just the same way as arseniuretted hydrogen, but the mirror given by Sb is not so volatile as that formed by As.

If hydrogen contains arseniuretted hydrogen, it also gives metallic arsenic when it burns, because in the reducing flame of hydrogen the oxygen attracted combines entirely with the hydrogen and not with the arsenic, so that if a cold object, such as a piece of china, be held in the hydrogen flame the arsenic will be deposited upon it as a metallic spot.[34]

The most common compound of arsenic is the solid and volatile **arsenious anhydride**, As_2O_3, which corresponds with phosphorous and nitrous anhydrides. This very poisonous, colourless, and sweet-tasting substance is generally known under the name of arsenic, or **white arsenic.** The corresponding hydrate is as yet unknown; its solutions, when evaporated, yield crystals of arsenious anhydride. It is chiefly prepared for the dyer, and is also used as a vermin-killer, and sometimes in medicine; it is a product from which all other compounds of arsenic can be prepared. It is obtained as a by-product in roasting cobalt

---

[34] This spot, or the metallic ring which is deposited on the heated tube, may easily be tested as to whether it is really due to arsenic or proceeds from some other substance reduced in the hydrogen flame—for instance, carbon or antimony. The necessity for distinguishing arsenic from antimony is all the more frequently encountered in medical jurisprudence, from the fact that preparations of antimony are very frequently used as medicine, and antimony behaves in the hydrogen apparatus just like arsenic, and therefore in making an investigation for poisoning by arsenic it is easy to mistake it for antimony. The best method to distinguish between the metallic spots of arsenic and antimony is to test them with a solution of sodium hypochlorite, free from chlorine, because this will dissolve arsenic and not antimony. Such a solution is easily obtained by the double decomposition of solutions of sodium carbonate and bleaching powder. A solution of potassium chlorate acts in the same manner, only more slowly. Further particulars must be looked for in analytical works.

Arseniuretted hydrogen, like phosphoretted hydrogen, is only slightly soluble in water, has no alkaline properties—that is, it does not combine with acids—and acts as a reducing agent. When passed into a solution of silver nitrate it gives a blackish-brown precipitate of metallic silver, the arsenic being oxidised. If acting on copper sulphate and similar salts, arseniuretted hydrogen sometimes forms arsenides—i.e., it reduces the metallic salt with its hydrogen, and is itself reduced to arsenic. Sulphuric, and even hydrochloric, acid reduces arseniuretted hydrogen to arsenic, and it is still more easily decomposed by arsenious chloride, and with phosphorous chloride it gives the compound PAs. Arseniuretted hydrogen gives metallic arsenic with an acid solution of arsenious anhydride (Tivoli).

and other ores containing arsenic. Arsenical pyrites are sometimes purposely roasted for the extraction of arsenious anhydride. When arsenical ores are burnt in the air, the sulphur and arsenic are converted into the oxides As_2O_3 and SO_2. The former is a solid at the ordinary temperature, and the latter gaseous, and therefore the arsenious anhydride is deposited as a sublimate in the cooler portion of the flues through which the vapours escape from the furnace. It collects in condensing chambers specially constructed in the flues. The deposit is collected, and after being distilled gives arsenious anhydride in the form of a vitreous non-crystalline mass. This is one of the varieties of arsenious anhydride, which is also known in two crystalline forms. When sublimed—i.e., when it passes rapidly from the state of vapour to the solid state—it appears in the regular system in the form of octahedra.[35] It is obtained in the same form when it is crystallised from acid solutions. The specific gravity of the crystals is 3·7. The other crystalline form (in prisms) belongs to the rhombohedral system, and is also formed by sublimation when the crystals are deposited on a heated surface, or when it is crystallised from alkaline solutions.[36]

Solutions of arsenious anhydride have a sweet metallic taste, and give **a feeble acid reaction.** Its solubility increases with the admixture of acids and alkalies. This as it were shows the property of arsenious anhydride of forming salts with acids and alkalies. And in fact compounds of it with hydrochloric acid (note 31), sulphuric anhydride

---

[35] According to Mitscherlich's determination, the vapour density of arsenious anhydride is 199 ($H=1$), that is, it answers to the molecular formula As_4O_6. Probably this is connected with the fact that the molecule of free arsenic contains As_4.

[36] Arsenious anhydride is obtained in an amorphous form after prolonged heating at a temperature near to that at which it volatilises, or, better still, by heating it in a closed vessel. It then fuses to a colourless liquid, which on cooling forms a transparent vitreous mass, whose specific gravity is only slightly less than that of the crystalline anhydride. On cooling, this vitreous mass undergoes an internal change, in which it crystallises and becomes opaque, and acquires the appearance of porcelain. The following difference between the vitreous and opaque varieties is very remarkable: when the vitreous variety is dissolved in strong and hot hydrochloric acid it gives crystals of the anhydride on cooling, and this crystallisation *is accompanied by the emission of light* (which is visible in the dark), and the entire liquid glows as the crystals begin to separate. The opaque variety does not emit light when the crystals separate from its hydrochloric acid solution. It is also remarkable that the vitreous variety passes into the opaque form when it is pounded—that is, under the action of a series of blows. Thus, several varieties of arsenious anhydride are known, but as yet they are not characterised by any special chemical distinctions, and even differ but little in their specific gravities, so that it cannot be said that the above differences are due to any isomeric transformation—that is, to an arrangement of the atoms in the molecule—but probably only depend on a difference in the distribution of the molecules, or, in other terms, are physical and not chemical variations. One part of the vitreous anhydride requires twelve parts of boiling water for its solution, or twenty-five parts at the ordinary temperature. The opaque variety is less soluble, and at the ordinary temperature requires about seventy parts of water for its solution.

(see further on), and with the alkali oxides are known.[37] If silver nitrate is added to a solution of arsenious anhydride, it does not give any precipitate unless a certain amount of the arsenious anhydride is saturated with an alkali—for instance, ammonia. It then gives a precipitate of silver arsenite, Ag_3AsO_3. This is yellow, soluble in an excess of ammonia, and anhydrous; it shows distinctly that arsenious acid is tribasic, and that it differs in this respect from phosphorous acid, in which only two atoms of hydrogen can be replaced by metals.[38] The feeble acid character of arsenious anhydride is confirmed by the formation of saline compounds with acids. In this respect the most remarkable example is the anhydrous compound with sulphuric acid, having the composition As_2O_3,SO_3. It is formed in the roasting of arsenical pyrites in those spaces where the arsenious anhydride condenses, a portion of the sulphurous anhydride being converted into sulphuric anhydride, SO_3, at the expense of the oxygen of the air. The compound in question forms colourless tabular crystals, which are

---

[37] Arsenious anhydride does not oxidise in air, either in a dry state or in solution, but in the presence of alkalies it absorbs oxygen from the air, and acts as a reducing agent. This probably is connected with the fact that arsenic acid is much more energetic than arsenious acid, and that it is arsenic acid which is formed by the oxidation of the latter in the presence of alkalies. Arsenious anhydride is easily reduced to arsenic by many metals, even by copper, and still more easily when ignited with carbon.

[38] The feebleness of the acid properties of arsenious anhydride is seen in the fact that if it be dissolved in ammonia water, and then a still stronger solution of ammonia be added, prismatic crystals separate having the composition of ammonium metarsenite, NH_4AsO_3. This ammonium salt deliquesces in air, and loses all its ammonia. The magnesium salt is tri-metallic, $Mg_3(AsO_3)_2$; it is insoluble in water, and is formed by mixing an ammoniacal solution of arsenious anhydride with an ammoniacal solution of a magnesium salt. It is insoluble even in ammonia, although it dissolves in an excess of an acid. Magnesium hydroxide gives the same salt with arsenious solutions, and hence magnesia is one of the best antidotes for arsenic poisoning. **The arsenites of copper** are much used in the manufacture of colours, more especially of pigments. They are distinguished by their insolubility in water and by their remarkably vivid green colour, but at the same time by their poisonous character. Not only do such pigments applied to wall papers or other materials easily dust off from them, but they give exhalations containing AsH_3. The cupric salts, CuX_2, when mixed with an alkaline solution of arsenious acid, give a green precipitate of a copper salt called *Scheele's green.* Its composition is probably $CuHAsO_3$. Ammonia dissolves it, and gives a colourless solution, containing cuprous arsenate—that is, the cupric compound is reduced and the arsenic subjected to oxidation. The so-called *Schweinfurt's green* was still more used, especially in former times; it is an insoluble green cupric salt, which resembles the preceding in many respects, but has a different tint. It is prepared by mixing boiling solutions of arsenious acid and cupric acetate. Arsenious acid forms with **ferric hydroxide**, $FeAsO_3$, an insoluble compound; and this is the reason why freshly precipitated oxide of iron is employed as an *antidote for arsenic.* The freshly precipitated oxide of iron, taken immediately after poisoning by arsenic, converts the arsenious acid into an insoluble state, by forming a compound on which the acids of the stomach have no action, so that the poisoning cannot proceed. It is remarkable that the inhabitants of certain mountainous countries accustom themselves to taking arsenic, which, according to their experience, helps to overcome the fatigue of mountain ascents.

decomposed by water with formation of sulphuric acid and arsenious anhydride.[39]

Antimony (stibium), Sb = 120, is another analogue of phosphorus. In its external appearance and the properties of its compounds it resembles the metals still more closely than arsenic does. In fact, antimony has the appearance, lustre, and many of the characteristic properties of the metals. Its oxide, Sb_2O_3, exhibits the earthy appearance of rust or of lime, and has distinctly basic properties, although it corresponds with nitrous and phosphorous anhydride, and is able, like them, to give saline compounds with bases. At the same time antimony presents, in the majority of its compounds, a complete analogy with phosphorus and arsenic. Its compounds belong to the types SbX_3 and SbX_5 It is found in nature chiefly in the form of sulphide, Sb_2S_3. This substance sometimes occurs in large masses in mineral veins and is known in mineralogy under the name of antimony glance or **stibnite,** and commercially as **antimony** (Chap. XX., note 29). The most abundant deposits of antimony ore occur in Portugal (near Oporto on the Douro). Besides which antimony partially or totally replaces arsenic in some minerals; thus, for example, a compound of antimony sulphide and arsenic sulphide with silver sulphide is found in red silver ore. But in any case antimony is a rather rare metal found in few localities. In Russia it is known to occur in Daghestan in the Caucasus. It is extracted chiefly for the preparation of alloys with lead and tin, which are used for casting printing type.[40] Some of its compounds are also used in medicine, the most important in this respect being antimony pentasulphide, Sb_2S_5 (*sulfur auratum antimonii*), and tartar emetic, which is a double salt derived from tartaric acid and has the composition $C_4H_4K(SbO)O_6$. Even the native antimony sulphide is used in large quantities as a purgative for horses and dogs. Metallic antimony is extracted from the glance, Sb_2S_3, by roasting, when the sulphur burns away and the antimony oxidises, forming the oxide Sb_2O_3, which is then heated with charcoal, and thus reduced to a

---

[39] Adie (1889) obtained compounds of As_2O_3 with 1, 2, 4, and 8 SO_3 by the direct action of ordinary and Nordhausen sulphuric acid upon As_2O_3. Weber had previously obtained As_2O_3,SO_3 (which disengages SO_3 at 225°), and also As_2O_3,nSO_3 (where $n=8$, 6, and 8), by the action of the vapours of SO_3 upon As_2O_3. The compound $As_2O_3,8SO_3$ loses SO_3 at 100°. Oxide of antimony, Sb_2O_3, gives similar compounds. Adie (1891) also obtained (by the action of SO_3 upon H_3PO_4) a compound $H_3PO_4,3SO_3$ in the form of a viscous liquid decomposed by water.

[40] Printer's type consists of an alloy known as 'type-metal,' containing usually about 15 parts of antimony to 85 parts of lead; sometimes (for example, for stereotypes) from 10 to 15 per cent. of Bi or 8 per cent. of Sn and even Cu is added. The hardness of the alloy, which is essential for printing, evidently depends upon the presence of antimony; but an excess must be avoided, since this renders the alloy brittle, and the type after a time loses its sharpness.

metallic state. The reduction may be carried on in the laboratory on a small scale by fusing the sulphide with iron, which takes up the sulphur.[40a]

Metallic antimony has a white colour and a brillant lustre; it remains untarnished in the air, for the metal does not oxidise at the ordinary temperature. It crystallises in rhombohedra, and always shows a distinctly crystalline structure which gives it quite a different aspect from the majority of the metals yet known. Antimony is brittle, so that it is easily powdered; its specific gravity is 6·7, it melts at about 629·5°, but only volatilises at a bright-red heat. When heated in the air—for instance, before the blowpipe—it burns and gives white odourless fumes, consisting of the oxide. This oxide is termed **antimonious oxide**, although it might as well be termed antimonious anhydride. It is given the first name because in the majority of cases its compounds with acids are used, but it forms compounds with the alkalies just as easily.

Antimonious oxide, like arsenious anhydride, crystallises either in regular octahedra or in rhombic prisms; its specific gravity is 5·56; when heated it becomes yellow and then fuses, and when further heated in air it oxidises, forming an oxide of the composition Sb_2O_4. Antimonious oxide is insoluble in water and in nitric acid, but it easily dissolves in strong hydrochloric acid and in alkalies, as well as in tartaric acid or solutions of its acid salts. When dissolved in the latter it forms tartar emetic. It is precipitated from its solutions in alkalies and acids (by the action of acids on the former and alkalies on the latter). It occurs native but rarely. As a base it gives salts of the type $SbOX$ (as if the basic salts$=SbX_3,Sb_2O_3$) and hardly ever forms salts, SbX_3. In the antimonyl salts, $SbOX$, the group SbO is univalent, like potassium or silver. The oxide itself is $(SbO)_2O$, the hydroxide $SbO(OH)$, &c.; tartar emetic is a salt in which one hydrogen of tartaric acid, $C_2H_4(CO_2H)_2$ is replaced by potassium and the other by antimonyl, SbO. Antimonious oxide is very easily separated from its salts by any base, but it must be observed that this separation does not take place in the presence of tartaric acid, owing to the pro-

---

[40a] Antimony is prepared in a state of greater purity by heating with charcoal the oxide obtained by the action of nitric acid on the impure commercial metallic antimony. This is based on the fact that by the action of the acid, antimony forms the oxide Sb_2O_3, which is but slightly soluble in water. The arsenic, which is nearly always present, forms soluble arsenious and arsenic acids, and remains in solution. The purest antimony is easily obtained from tartar emetic, by heating it with a small quantity of nitre. Metallic antimony also occurs, although rarely, native; and as it is very easily obtained, it was known to the alchemists of the fifteenth century. Very pure metallic antimony may be deposited by the electric current from a solution of antimonious sulphide in sodium sulphide after the addition of sodium chloride to the solution.

perty of tartaric acid of forming a soluble double salt—i.e., tartar emetic.[41]

If metallic antimony, or antimonious oxide, is oxidised by an excess of nitric acid and the resultant mass carefully evaporated to dryness, **metantimonic** acid, $SbHO_3$, is formed. Its corresponding potassium salt, $2SbKO_3,5H_2O$, is prepared by fusing metallic antimony with one-fourth its weight of nitre and washing the resultant mass with cold water. This potassium salt is only slightly soluble in water (in 50 parts) and the sodium salt still less so. An ortho-acid, SbH_3O_4, also appears to exist;[41a] it is obtained by the action of water on antimony pentachloride, but it is very unstable, like the pentachloride, $SbCl_5$, itself, which easily gives up Cl_2, leaving antimony trichloride, $SbCl_3$, and this is decomposed by water, forming an oxychloride—$SbOCl$, only slightly soluble in water. When antimonic acid is heated to an incipient red heat, it parts with water and forms the anhydride, Sb_2O_5, of a yellow colour and specific gravity 6·5.[42]

[41] As antimonious oxide answers to the type SbX_3, it is evident that compounds may exist in which antimony will replace three atoms of hydrogen; such compounds have been to some extent obtained, but they are easily converted by water into substances corresponding with the ordinary formulæ of the compounds of antimony. Thus tartar emetic, $C_4H_4(SbO)KO_6$, loses water when heated, and forms $C_4H_2SbKO_6$—that is, tartaric acid, $C_4H_6O_6$, in which one atom of hydrogen is replaced by potassium and three by antimony. But this substance is reconverted into tartar emetic by the action of water. A similar compound is seen in that **intermediate oxide of antimony** which is formed when antimonious oxide is heated in air; its composition is SbO_2 or Sb_2O_4. This oxide may be regarded as ortho-antimonic acid, $SbO(HO)_3$, in which three atoms of hydrogen are replaced by antimony—i.e., $SbO(SbO_3) = Sb_2O_4$. Oxide of antimony is also formed when antimonic acid is ignited; it then loses water and oxygen, and gives this intermediate oxide as a white infusible powder, of sp. gr. 6·7. It is somewhat soluble in water, and gives a solution which turns litmus paper red.

[41a] Beilstein and Blaese (1889), after preparing many salts of antimonic acid, came to the conclusion that it is monobasic, but all the salts still contain water, so that their general type is mostly $MSbO_3,3H_2O$, M being, for example, Li, Hg (salts of the suboxide), ½ Pb, &c. The type of the ortho-salts, M_3SbO_4, is quite unknown, although it is reproduced in the thio-compounds, for instance, Schlippe's salt, Na_3SbS_4; but this salt also contains water of crystallisation, $9H_2O$ (Chap. XX., note 29).

[42] Among the other compounds of antimony, **antimoniuretted hydrogen**, SbH_3 (by the action of acids upon the alloy Sb_2Mg_3) resembles arseniuretted hydrogen in its mode of formation and properties (it splits up at 150°, Brunn, 1890; when liquefied, it boils at $-17°$ and solidifies at $-28°$), whilst the halogen compounds differ in many respects from those of arsenic. When chlorine is passed over an excess of antimony powder, it forms **antimony trichloride**, $SbCl_3$, but if the chlorine be in excess it forms the pentachloride, $SbCl_5$. The trichloride is a crystalline substance which melts at 72° and distils at 230°, whilst the pentachloride is a yellow liquid, which splits up into chlorine and the trichloride when heated; at 140° it begins to give off chlorine abundantly, and this carries away the vapour of the trichloride with it; at 200° the decomposition is complete, and pure antimonious chloride alone passes over. This property of antimony pentachloride has caused it to be applied in many cases for the transference of chlorine; all the more so, because when it has given up its chlorine, it leaves the trichloride, which is able to absorb a fresh amount of chlorine; and therefore many substances which are

The heaviest analogue of nitrogen and phosphorus is **bismuth**, Bi=208. Here, as in the other groups, the basic, metallic properties increase with the atomic weight. Bismuth does not give any hydrogen compound, and the highest oxide, Bi_2O_5, is a very feeble acid oxide. Bismuthous oxide, Bi_2O_3, is a base, and bismuth itself a perfect metal. To explain the other properties of bismuth it must further be remarked that it follows mercury, thallium, and lead, whose atomic weights are near to that of bismuth, and that therefore it resembles them and more especially its nearest neighbour, lead. Although PbO and PbO_2 represent types different from Bi_2O_3 and Bi_2O_5, they resemble them in many respects, even in their external appearance, and moreover the lower oxides both of Pb and Bi are basic and the higher ones, which easily evolve oxygen, acid. But judging even by the formula, Bi_2O_3 is a more feeble base than PbO. They both easily give basic salts.

Bismuth, like P, As, and Pb, forms compounds of two types, BiX_3

unable to react directly with gaseous chlorine do so with antimony pentachloride, and in the presence of a small quantity of it chlorine will act on them, just as oxygen is able, in the presence of nitrogen oxides, to oxidise substances which could not be oxidised by means of free oxygen. Thus carbon bisulphide is not acted on by chlorine at low temperatures—this reaction requires a high temperature—but in the presence of antimony pentachloride its conversion into carbon tetrachloride takes place at low temperatures. Antimony tri- and penta-chlorides, having the character of chloranhydrides, fume in air, attract moisture, and are decomposed by water, forming antimonious and antimonic acids. But in the first action of water the trichloride does not evolve all its chlorine as hydrochloric acid, which is intelligible in view of the fact that antimonious anhydride is also a base, and is therefore able to react with acids; indeed antimony sulphide dissolved in an excess of hydrochloric acid (hydrogen sulphide is evolved) gives an aqueous solution of antimony trichloride, which, when carefully distilled, even gives the anhydrous compound. Antimony trichloride is only decomposed by an excess of water, and then not completely, for with a large quantity of water it forms *powder of algaroth*—i.e., antimony oxychloride. The first action of water consists in the formation of **oxychloride**, SbOCl, but the composition of the product varies with the relative amount of water, between the limits SbOCl and $Sb_4O_5Cl_2$. The latter compound is, as it were, a basic salt of the former, because its composition is $2(SbOCl)Sb_2O_3$.

With bromine and iodine, antimony forms compounds similar to those with chlorine. Antimonious bromide, $SbBr_3$, crystallises in colourless prisms, melts at 94°, and boils at 270°; antimonious iodide, SbI_3, forms red crystals of sp. gr. 5·0; antimony trifluoride, SbF_3, separates from a solution of antimonious oxide in hydrofluoric acid, and SbF_5 is formed by a similar treatment of antimonic acid. The latter gives easily soluble double salts with the fluorides of the metals of the alkalies.

De Haën (1887) obtained very stable double soluble salts, SbF_3,KCl (100 parts of water dissolve 57 parts of salt), SbF_3,K_2SO_4, &c., which he proposed to make use of in the arts as very easily crystallisable and soluble salts of antimony. Engel, by passing hydrochloric acid gas into a saturated solution of antimonious chloride at 0°, obtained a compound $HCl,2SbCl_3,2H_2O$, and with the pentachloride a compound $SbCl_5,5HCl,10H_2O$. Bismuth trichloride, $BiCl_3$, gives a similar compound. Ditte and Metzner (1892) showed that Sb and Bi dissolve in hydrochloric acid only owing to the participation of the oxygen of the air or of that dissolved in the acid.

and BiX_5,[43] which completely recall the two types we have already established for the compounds of lead. Just as in the case of lead, the type PbX_2 is basic, stable, easily formed, and passes with difficulty into the higher and lower types, which are unstable, so also in the case of bismuth the type of combination BiX_3 is the usual basic form. The higher type of combination, BiX_5,[44] behaves in fact toward this stable type, BiX_3, in exactly the same manner as lead dioxide does to the monoxide; and bismuthic acid is obtained by the action of chlorine on bismuth oxide suspended in water, in exactly the same way as lead dioxide is obtained from lead oxide. It is an oxidising agent like lead dioxide, and even the acid character in bismuthic acid is only slightly more developed than in lead dioxide. Here, as in the case of lead (minium), intermediate compounds are easily formed in which the bismuth of the lower oxide plays the part of a base combined with the acid which is formed by the higher form of the oxidation of bismuth.

In nature, bismuth occurs in only a few localities and in small quantities, most frequently in a native state, and more rarely as oxide and as a compound of bismuth sulphide with the sulphides of other metals, and sometimes in gold ores. It is extracted from its native ores by simple fusion in the furnace shown in fig. 96. This furnace contains an inclined iron retort, into the upper extremity of which the ore is charged, and the molten **metal** flows from the lower extremity. It is

---

[43] Metallic bismuth is very easily obtained when the compounds of the oxide are reduced by powerful reducing agents, but when less powerful reducing agents—for example, stannous oxide—are taken, bismuth suboxide is formed as a black crystalline powder. It is a compound of the type BiX_2, its composition being BiO; it is decomposed by acids into the metal and oxide, which passes into solution.

[44] The type BiX_5 is represented by the pentoxide, Bi_2O_5, its metahydrate, Bi_2O_5,H_2O, or $BiHO_3$, known as bismuthic acid, and the pyrohydrate, $Bi_2H_4O_7$. **Bismuth pentoxide** is obtained by a prolonged passage of chlorine through a boiling solution of potassium hydroxide (sp. gr. 1·38), containing bismuth oxide in suspension; the precipitate is washed with water, with boiling nitric acid (but not for long, as otherwise the bismuthic acid is decomposed), then again with water, and finally the resultant bright red powder of the hydrate, $BiHO_3$, is dried at 125°. The prolonged action of nitric acid on bismuthic anhydride, Bi_2O_5, results in the formation of the compound Bi_2O_4,H_2O, which decomposes in moist air, forming Bi_2O_3. The density of bismuthic anhydride is 5·10, that of the tetroxide, Bi_2O_4, 5·60, and that of bismuthic acid, $BiHO_3$, 5·75. **Pyrobismuthic acid**, $Bi_2H_4O_7$, forms a brown powder, which loses a portion of its water at 150°, and decomposes on further heating, with the evolution of oxygen and water. It is obtained by the action of potassium cyanide on a solution of bismuth nitrate. The meta-salts of bismuthic acid are known; for example, $KBiO_3$. They generally occur, however, in combinations with meta-bismuthic acid itself. Thus, André (1891) took a solution of the double salt of $BiBr_3$ and KBr, treated it with bromine after adding ammonia, and obtained a red-brown precipitate, which after being washed (for several weeks) had the composition $KBiO_3$, $HBiO_3$. When washed with dilute nitric acid this salt gave bismuthic acid.

refined by re-melting, and the pure metal may be obtained by dissolving in nitric acid, decomposing the resultant salt with water, and reducing the precipitate by heating it with charcoal. Bismuth is a metal which crystallises very well from a molten state. Its specific gravity is 9·8; it melts at 269°, and if it is melted in a crucible, allowed to cool slowly, and the crust broken and the remaining molten liquid poured out, perfect rhombohedral crystals of bismuth are obtained on the sides of the crucible.[44a] It is brittle, has a grey-coloured fracture with a reddish lustre, is not hard, and is but very slightly ductile and malleable; it volatilises at a white heat and easily oxidises, but it does not become tarnished or oxidised at the ordinary temperature. It recalls antimony and lead in many of its properties. When oxidised in air, or when the nitrate is ignited, bismuth forms the **oxide**, Bi_2O_3, as a white powder which fuses when heated and resembles massicot. The addition of an excess of caustic potash to a solution of a bismuthous salt gives a white precipitate of the hydroxide, BiO(OH), which loses its water and gives the anhydrous oxide when boiled with a solution of caustic potash. Both the hydroxide and oxide easily dissolve in acids and form bismuthous salts.

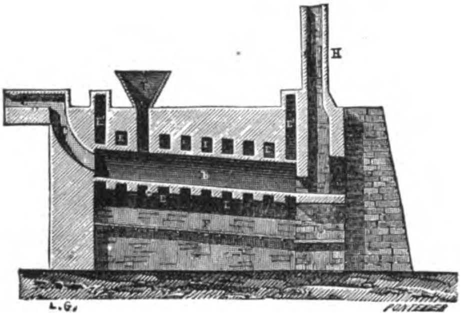


FIG. 96.—Furnace used for the extraction of bismuth from its ores.

Bismuthous oxide, Bi_2O_3, is a feeble and unenergetic base. The ortho-hydroxide, $Bi(OH)_3$, parts with water and forms a metahydroxide (bismuthyl hydroxide), BiO(OH). Both of these hydroxides have their corresponding saline compounds of the compositions BiX_3 and BiOX. And the form BiOX is nothing else than the type of the basic salt, because $3ROX = RX + R_2O_3$. Many bismuth salts are formed according to the type BiOX, for instance, the carbonate, $(BiO)_2CO_3$, which corresponds with the other carbonates M_2CO_3. It is obtained as a white precipitate when a solution of sodium carbonate is added to a solution

---

[44a] Hérard (1889) obtained a peculiar variety of bismuth by heating pure crystalline bismuth to a bright red heat in a stream of nitrogen. A greenish vapour was deposited in the cooler portions of the apparatus in the form of a grey powder, which, under the microscope, had the appearance of minute globules. An atmosphere of nitrogen is necessary for this transformation; other gases such as hydrogen and carbonic oxide do not favour the transition. The resultant amorphous bismuth fuses at 410° (the crystalline variety at 269°), and has the sp. gr. 9·483. (Does it not contain a nitride?)

of a bismuth salt.[45] The compound radicle BiO is not a special natural grouping, as it was formerly represented to be; it is simply a mode of expression for showing the relation between the compound in question and the compounds of other oxides.

Three **salts of nitric acid** are known containing bismuthous oxide. If metallic bismuth or its oxide is dissolved in nitric acid, it forms a colourless transparent solution containing a salt which separates in large transparent crystals containing $Bi(NO_3)_3,5H_2O$.[45a] When heated at 72° these crystals melt, and at 75° already deposit an insoluble basic salt whose empirical formula is $Bi_2N_2H_2O_9$. If the preceding salt belongs to the type BiX_3, this one should belong to the form BiOX, because it corresponds with $BiO(NO_3)+Bi(HO)_2(NO_3)$. This salt may be heated to 150° without change. When the first colourless crystalline salt dissolves in water **it is decomposed.** There is no decomposition if an excess of acid is added to the water—that is to say, the salt is able to exist in an acid solution without decomposing, without separation of the so-called basic salt—but by itself it cannot be kept in solution; water decomposes this salt, acting on it like an alkali. In other words, the basic properties of bismuthic oxide are so feeble that even water acts by taking up a portion of the acid from it. Here we see one of the most striking facts, long since observed, confirming that action of water on salts about which we have spoken in Chapter X. and elsewhere. This action of water may be expressed thus:—$BiX_3+2H_2O=Bi(OH)_2X+2XH$. A salt of the type $Bi(OH)_2X$ is obtained in the precipitate. But if the quantity of acid, HX, be increased, the salt BiX_3 will again be formed and will pass into solution. The quantity of the salt BiOX which passes into solution on the addition of a given quantity of acid depends indisputably on the amount (mass) of water (Muir). The solution, which is perfectly transparent with a small amount of water, becomes cloudy and deposits the salt of the type BiOX, when diluted. The white flaky precipitate of $Bi(OH)_2NO_3$ formed from the normal salt, $Bi(NO_3)_3$, by mixing it with five parts of water, and

[45] Basic bismuth carbonate is employed for whitening the skin (veloutine).

[45a] Rutten (1902) showed that oxide of bismuth, or the above-mentioned neutral salt, under the action of an excess of monohydrated nitric acid (at the ordinary temperature), forms a crystalline powder containing far less water: $Bi_2(NO_3)_6,3H_2O$. Rutten also observed that if sufficient water is added to strong HNO_3 to form an acid capable of dissolving the pentahydrated salt without decomposing it, and then strong nitric acid is added to the saturated solution, it forms a transparent, gelatinous, colloidal mass, which subsequently deposits the above less-hydrated crystals. The system composed of oxide of bismuth, nitric acid, and water presents a most instructive instance of chemical equilibrium in dependence upon the pressure, temperature, and the relative amounts of the component substances and their combination and state (phase).

in general with a small amount of water, is used in medicine under the name of magisterium bismuthi.[46]

Metallic bismuth is used in the preparation of fusible alloys. The addition of bismuth to many metals renders them very hard, and at the same time generally lowers their melting-points to a considerable extent. Thus Wood's metal, which contains one part of cadmium, one of tin, two of lead, and four of bismuth, fuses at about 60°.[47] Rose's alloy, which fuses at 96°, contains two parts of Bi, one of Sn and one of Pb; and in general many alloys composed of bismuth, tin, lead, and antimony melt below or about the boiling-point of water.

Just as in group II., side by side with the elements zinc, cadmium, and mercury in the uneven series, we found calcium, strontium, and barium in the even series; and as in group IV., parallel to silicon, germanium, tin, and lead, we noticed thallium, zirconium, cerium, and thorium; so also in group V. we find, beside the elements of the uneven series P, As, Sb, and Bi, a series of analogues in the even series, which, with a certain degree of similarity (mainly quantitative, or relative to the atomic weights), also present a series of particular (qualitative) independent points of distinction. In the even series **vanadium, niobium,** and **tantalum** are known. Just as bismuth is similar in many respects to its neighbour lead, so also do V, Nb, and Ta resemble their nearest neighbours in the other groups, Ti, Zr, Cr, Mo, and W, even in their external appearance, not to mention the nature of their com-

---

[46] With an excess of water a further quantity of acid is separated and a still more basic salt formed. The ultimate product, on which an excess of water has apparently no action whatever, is a substance having the composition $BiO(NO_3),BiO(OH)$. If we refer all the bismuthous compounds to the type, Bi_2X_6, we shall obtain the following expression for the composition of the nitrates: normal salt, $Bi_2(NO_3)_6$; first basic salt, $Bi_2O(OH)_2(NO_3)_2$; magisterium bismuthi, $Bi_2(OH)_4(NO_3)_2$, and the limiting form $Bi_2O_2(OH)(NO_3)$.

The general character of bismuthous oxide in its compounds is well exemplified in the nitrate; **bismuthous chloride**, $BiCl_3$, which is obtained by heating bismuth in chlorine, or by dissolving it in aqua regia, and then distilling without access of air, is also decomposed by water in exactly the same manner, and forms basic salts—for instance, first, BiOCl, &c. Bismuth chloride boils at 447°, and its formula is probably $BiCl_3$. Polymerisation may take place in some compounds and not in others. A volatile compound of the composition $Bi(C_2H_5)_3$ is also known as a liquid which is insoluble in water and decomposes with explosion when heated at 130°. Double salts containing chloride of bismuth are: $2(KCl),BiCl_3,2H_2O$ (from a solution of Bi_2O_3 and KCl in hydrochloric acid) and $KCl,BiCl_3,H_2O$. Bigham (1892) also obtained $KBr(SO_4)_2$ in tabular crystals by treating the above-named double salt with strong sulphuric acid. The composition of this salt recalls that of alum.

[47] As this alloy is fusible, it may be employed in the place of mercury in many physical experiments conducted at or above 70°, and it offers the advantage that its vapour has no appreciable pressure (mercury at 100°, 0·75 mm). Bismuth expands in passing into a molten state, but it has a temperature of maximum density. According to Luedeking the mean coefficient of expansion of liquid bismuth is 0·0000442 (between 270° and 303°), and that of solid bismuth 0·0000411.

pounds, naturally taking into account the differences of type corresponding with the different groups. The occurrence in group V. determines the type of the oxides, R_2O_3 and R_2O_5, and the development of an acid character in the higher oxides. The occurrence in the even series determines the absence of volatile compounds, RH_3, for these metals, and a more basic character of the oxides of a given composition than in the uneven series, &c. Vanadium, niobium, and tantalum belong to the category of rare metals, and are exceedingly difficult to obtain pure, owing more especially to their similarity to, and occurrence with, chromium, tungsten, and other metals, and also in combination among themselves; it is, therefore, natural that they have been far from completely studied, although since 1860 chemists have devoted not a little time to their investigation. The researches carried out by Marignac, at Geneva, on niobium, and by Sir Henry Roscoe, at Manchester on vanadium deserve special attention.[48] The undoubted qualitative resemblance between the compounds of vanadium and those of chromium, as well as the want of completeness in the knowledge of the compounds of vanadium, long caused its oxides to be considered analogous in atomic composition to those formed by chromium. The higher oxide of vanadium was therefore supposed to have the formula VO_3. But, as a matter of fact, the chemical analogy of the elements does not hold in one direction only; vanadium is at one and the same time the analogue of chromium, group VI., and also the analogue of phosphorus, arsenic, and antimony; just as bismuth is related to both lead and antimony. We should have to extend our description considerably if we wished to give the complete history, even of vanadium alone, not to mention niobium and tantalum, especially as some of the questions concerning the compounds of these elements have not yet been fully elucidated. We shall therefore limit ourselves to pointing out the most important features in the history of these elements, since the minerals themselves in which they occur are exceedingly rare and only accessible to a few investigators.

An important point in the history of the members of this group is the circumstance that they form volatile compounds with chlorine, similar to the compounds of the elements of the phosphorus group, namely, to those of the type RX_5. The vapour densities of the compounds of these elements were determined, and served as the most important basis for the explanation of the molecular composition of

---

[48] Roscoe demonstrated the quantitative analogy of the vanadium and phosphorus compounds and the qualitative analogy of the vanadium and chromium compounds, which was an unexpected and important discovery at the time. The periodic law explained and generalised these relations.

these molecules. In this we see the power of general and fundamental laws, like that of Avogadro-Gerhardt. An oxychloride, $VOCl_3$, is known for vanadium, which is the perfect analogue of phosphorus oxychloride. It was formerly considered to be vanadium chloride, for just as in the case of uranium (Chap. XXI.), its lower oxide, VO, was considered to be the metal, because it is exceedingly difficultly reduced—even potassium does not remove all the oxygen, besides which it has a metallic appearance, and decomposes acids like a metal; in a word, it simulates a metal in every respect. **Vanadium oxychloride** is obtained by heating the trioxide, V_2O_3, mixed with charcoal, in a current of hydrogen; the lower oxide of vanadium is then formed, and this, when heated in a current of dry chlorine, gives the oxychloride $VOCl_2$ as a reddish liquid which does not act on sodium and may be purified by distillation over this metal. It fumes in the air, giving reddish vapours; it reacts on water, forming hydrochloric and vanadic acids; hence it is very similar, on the one hand, to phosphorus oxychloride, and, on the other hand, to chromium oxychloride, CrO_2Cl_2 (Chap. XXI.). It is of a yellow colour, its specific gravity is 1·83, it boils at 120°, and its vapour density is 86 with respect to hydrogen; therefore the above formula expresses its molecular weight.[49]

Vanadic anhydride, V_2O_5, is obtained either in small quantities from certain clays where it accompanies the oxides of iron (hence some sorts of iron contain vanadium) and phosphoric acid, or from the rare minerals: volborthite, $CuHVO_4$, or basic vanadate of copper; vanadinite, $PbCl_2,3Pb_3(VO_4)_2$; lead vanadate, $Pb_3(VO_4)_2$, &c.[49a] The latter salts are carefully ignited for some time with one-third of their weight of nitre, the fused mass being powdered and boiled in water; the yellow solution obtained contains potassium vanadate. The solution is neutralised with acid, and barium chloride added; a meta-salt, $Ba(VO_3)_2$, is then precipitated as an almost insoluble white powder, which gives a solution of vanadic acid when boiled with sulphuric acid.

---

[49] When vanadium oxychloride is heated with zinc in a closed tube at 400°, it loses a portion of its chlorine and forms a green crystalline mass of sp. gr. 2·88, which is deliquescent in air and has the composition $VOCl_2$. Only its vapour density is unknown, and it would be extremely important to determine whether its molecular composition is that given above, or whether it corresponds with the formula $V_2O_2Cl_4$. Another less volatile oxychloride, VOCl, is formed with it as a brown insoluble substance, which is, however, soluble in nitric acid like the preceding. Roscoe obtained a still lower chlorinated substance, namely, $(VO)_2Cl$; but it may only consist of a mixture of VO and VOCl. At all events, we here find a graduated series such as is met with in the compounds of very few other elements.

[49a] A mineral called Roscoelite rich in vanadium has been found in California. The fact that compounds of vanadium have been found in the mother liquors obtained in the manufacture of soda and beet-sugar shows that traces of this element are widely distributed in nature.

(The precipitate is at first yellow, as long as it remains amorphous, but it afterwards becomes crystalline and white.) The solution thus obtained is neutralised with ammonia, thus forming ammonium (meta-) vanadate, NH_4VO_3, which, when evaporated, gives colourless crystals, insoluble in water, containing sal-ammoniac; this salt is hence precipitated by adding solid sal-ammoniac to the solution.[49b] Ammonium vanadate, when ignited, leaves vanadic acid behind. In this it differs from the corresponding chromium salt, which is deoxidised into chromium oxide when ignited. In general, vanadic acid has but a slight oxidising action. It is reduced with difficulty, like phosphoric or sulphuric acid, and in this differs from arsenic and chromic acids. Vanadic acid, like chromic acid, separates from its solution as the anhydride V_2O_5, and not in a hydrous state. Vanadic anhydride, V_2O_5, forms a reddish-brown mass, which readily fuses and re-solidifies into transparent crystals having a violet lustre (another point of resemblance to chromic acid); it dissolves in water, forming a yellow solution with a slightly acid reaction.[50]

[49b] With peroxide of hydrogen, NH_4VO_4 is easily formed. It corresponds to the peroxide componnd, pervanadic acid, HVO_4, of the same type as persulphuric and per chromic acids (see following chapter.)

[50] Strong acids and alkalies dissolve vanadic anhydride in considerable quantities, forming yellow solutions. When it is ignited, especially in a current of hydrogen, it evolves oxygen and forms the lower oxides: V_2O_4 (acid solutions of a green colour, like the salts of chromic oxide), V_2O_3, and the lowest oxide, VO. The latter is the metallic powder which is obtained when vanadium oxychloride is heated in an excess of hydrogen, and was formerly mistaken for metallic vanadium. When a solution of vanadic acid is treated with metallic zinc it forms a blue liquid, which seems to contain this oxide. It acts as a reducing agent (and forms a close analogue to chromous oxide, CrO). Metallic **vanadium** can only be obtained from vanadium chloride which is quite free from oxygen. Moissan (1893) obtained it by reducing the oxide with carbon in the electric furnace, and considered it to be the most infusible of the metals in the series Pt, Cr, Mo, U, W, and V (he also obtained a compound of vanadium and carbon). The specific gravity of this metal is 5·5. It is of a greyish-white colour, is not decomposed by water, and is not oxidised in air, but burns when strongly heated, and can be fused in a current of hydrogen (perhaps forming a compound with hydrogen). It is insoluble in hydrochloric acid, but easily dissolves in nitric acid, and when fused with caustic soda forms sodium vanadate.

As regards the salts of vanadic acid, three different classes are known: the first correspond with metavanadic acid, $VMO = M_2OV_2O_5$, the second correspond with the dichromates—that is, have the composition $V_4M_2O_{11}$, which is equal to $M_2O + 2V_2O_5$—and the third with orthovanadic acid, VM_3O_4 or $3M_2O + V_2O_5$. The latter are formed when vanadic anhydride is fused with an excess of an alkaline carbonate.

Vanadic acid gives the so-called 'complex' acids (which are considered more fully in Chap. XXI. when speaking of Mo and W)—i.e., acids formed of two acids assimilated into one. Thus, Friedheim (1890) obtained phosphor-vanadic acid, and Schmitz-Dumont (1890) a similar arseno-vanadic acid. The former is obtained by heating V_2O_5 with syrupy phosphoric acid. The resultant golden-yellow tabular crystals have the composition $H_2O,V_2O_5,P_2O_5,9H_2O$, and there are corresponding salts—for example, $(NH_4)_2V_2O_5,P_2O_5$ with 8 and $7H_2O$, &c. These salts cannot be separated by crystallisation, so that there are 'complexes' of these acids in a whole series of salts (and also in nature). It may be supposed (Friedheim) that V_2O_5 here plays, as it were, the part of a

Niobium and tantalum [51] occur as acids in rare minerals, and are mainly extracted from tantalite and columbite, which are found in Bavaria, Finland, North America, and in the Urals. These minerals are composed of the ferrous salts of niobic and tantalic acids ; they contain about 15 per cent. of ferrous oxide in isomorphous mixture with manganous oxide, in combination with various proportions of tantalic and niobic anhydrides. These minerals are first fused with a considerable amount of potassium bisulphate, and the fused mass is boiled in water, which dissolves the ferrous and potassium salts and leaves an insoluble residue of impure niobic and tantalic acids. This raw product is then treated with ammonium sulphide, in order to extract the tin and tungsten, which pass into solution. The residue containing the acids (according to Marignac) is then treated with hydrofluoric acid, in which it entirely dissolves, and potassium fluoride is added to the resultant hot solution ; on cooling, a sparingly soluble double fluoride of potassium and tantalum separates out in fine crystals, while the much more soluble niobium salt remains in solution. The difference in the solubility of these double salts in water acidified with hydrofluoric acid (in pure water the solution becomes cloudy after a

---

base, or that these acids may be looked upon as double salts. Of the true double salts of vanadium (Nb and Ta), very many are known among the fluorides, such as $VF_3,2NH_4F$, $VOF_2,2NH_4F$, $VO_2F,3NH_4F$, &c. (Pettersson, Piccini, and Georgi, 1890–92). V_2O_3 also gives a double salt having the composition of an alum.

Vanadium was discovered at the beginning of this century by Del-Rio, and was afterwards investigated by Sefström, but it was only in 1868 that Roscoe established the above formulæ of the vanadic compounds.

[51] The researches made by Roscoe were preceded by those of Marignac in 1865, on the **niobium** and **tantalum compounds**, to which were also ascribed formulæ different from those now recognised. Tantalum was discovered simultaneously with vanadium by Hatchett and Ekeberg, and was afterwards studied by Rose, who in 1844 discovered niobium in it. Notwithstanding the numerous researches of Hermann (in Moscow), Kobell, Rose, and Marignac, there is as yet no certainty as to the purity of, and the properties ascribed to, the compounds of these elements. They are difficult to separate from each other, and especially from the cerite metals and titanium, &c., which accompany them. Before the investigations of Rose the highest oxide of tantalum was supposed to belong to the type TaX_6—that is, its composition was taken as TaO_3, and to the lower oxide was ascribed a formula TaO_2. Rose gave the formula TaO_2 to the higher oxide, and discovered a new element called niobium in the substance previously supposed to be the lower oxide. He even admitted the existence of a third element occurring together with tantalum and niobium, which he named pelopium, but he afterwards found that pelopic acid was only another oxide of niobium, and he considered it probable that the higher oxide of this element is NbO_2, and the lower Nb_2O_3. Hermann found that niobic acid which was considered pure contained a considerable quantity of tantalic acid, and besides this he admitted the existence of another special metallic acid, which he called ilmenic acid, after the locality (the Ilmen mountains of the Urals) of the mineral from which he obtained it. V. Kobell recognised still another acid, which he called dianic acid, and these diverse statements were only brought into agreement in the sixties by Marignac. He first of all indicated an accurate method for the separation of tantalic and niobic compounds, which are always obtained in admixture.

certain time) is so great that the tantalum compound requires 150 parts of water for its solution, and the niobium compound only 13 parts. The Greenland columbite (specific gravity 5·36) contains only niobic acid, and that from Bodenmais, Bavaria (specific gravity 6·06), almost equal quantities of tantalic and niobic acids. Having isolated tantalic and niobic salts, Marignac found that the relation between the potassium and fluorine in them is very variable—that is, that there exist various double salts of fluoride of potassium with the fluorides of the metals of this group, but that with an excess of hydrofluoric acid both the tantalum and niobium compounds contain seven atoms of fluorine to two of potassium, whence it must be concluded that the simplest formula for these double salts will be $K_2RF_7=RF_5,2KF$; that is, that the type of the higher compounds of niobium and tantalum is RX_5, and is hence similar to phosphoric acid. A chloride, $TaCl_5$, may be obtained from pure tantalic acid by heating it with charcoal in a current of chlorine. This is a yellow crystalline substance, which melts at 211°, and boils at 241°; its vapour density with respect to hydrogen is 180, as would follow from the formula $TaCl_5$. It is completely decomposed by water into tantalic and hydrochloric acids. **Niobium pentachloride** may be prepared in the same manner; it fuses at 194°, and boils at 240°. When treated with water this substance gives a solution containing niobic acid, which only separates out on boiling the solution. Delafontaine and Deville found its vapour density to be 9·3 (air = 1), as is indicated by its formula $NbCl_5$.[52] In general, vanadium, niobium and tantalum form, as far as we know,

---

[52] If niobic acid is mixed with a small quantity of charcoal and ignited in a stream of chlorine, a difficultly fusible and difficultly volatile oxychloride, $NbOCl_3$, separates. The vapour density of this compound with respect to air is 7·5, and this vapour density completely confirms the accuracy of the formulæ given by Marignac, and indicates the quantitative analogy between the compounds of niobium and tantalum, and those of phosphorus and arsenic, and consequently also of vanadium. In their qualitative relations, as is evident also from the correspondence of the atomic weights, the compounds of tantalum and niobium exhibit a great analogy with those of molybdenum and tungsten. Thus, zinc, when acting on acid solutions of tantalic and niobic compounds, gives a blue coloration, exactly as it does with those of tungsten and molybdenum (also titanium). These acids form the same large number of salts as those of tungsten and molybdenum. The anhydrides of the acids are also insoluble in water, but are sometimes held in solution as colloids, just like those of titanic and molybdic acids. Furthermore, niobium is in every respect the nearest analogue of molybdenum, and tantalum of tungsten. **Niobium** is obtained by reducing the double fluoride of niobium and sodium with sodium. It is difficult to obtain in a pure state. It is a metal on which hydrochloric acid acts with some energy, as also does hydrofluoric acid mixed with nitric acid, and also a boiling solution of caustic potash. **Tantalum,** which is obtained in exactly the same way, is a much heavier metal. It is infusible, and is only acted on by a mixture of hydrofluoric and nitric acids. Rose, in 1868, showed that in the reduction of the double fluoride, $NbF_5,2KF$, by sodium, a greyish powder is obtained after treating with water. The specific gravity of this powder is 6·3, and he considers it to be niobium

compounds corresponding to the types RX, RX_2, RX_3, RX_4 and RX_5, and this multiplicity of forms, which recalls manganese and nitrogen, renders the investigation of these very rare elements somewhat difficult.

---

hydride, NbH. Neither did he obtain metallic niobium when he reduced with magnesium and aluminium, but an alloy, Al_3Nb, having a sp. gr. of 4·5.

Niobium, so far as is known, unites in three proportions with oxygen. NbO, which is formed when $NbOF_3,2KF$ is reduced by sodium; NbO_2, which is formed by igniting niobic acid in a stream of hydrogen, and niobic anhydride, Nb_2O_5, a white infusible substance, which is insoluble in acids and has a specific gravity of 4·5. Tantalic anhydride closely resembles niobic anhydride, and has a specific gravity of 7·2. **The tantalates and niobates** present the type of ortho-salts—for example, $Na_2HNbO_4,6H_2O$, and also of pyro-salts, such as $K_3HNb_2O_7,6H_2O$, and of meta-salts—for example, $KNbO_3,2H_2O$. And, besides these, they give salts of a more complex type, containing a larger amount of the elements of the anhydride; thus, for instance, when niobic anhydride is fused with caustic potash it forms a salt which is soluble in water, and crystallises in monoclinic prisms, having the composition $K_8Nb_6O_{19},16H_2O$. There is a perfectly similar isomorphous salt of tantalic acid. Tantalite is a salt of the type of metatantalic acid, $Fe(TaO_3)_2$. The composition of yttrotantalite appears to correspond with that of orthotantalic acid.

CHAPTER XX

SULPHUR, SELENIUM, AND TELLURIUM

THE acid character of the higher oxides RO_3 of the elements of group VI. is still more clearly defined than that of the higher oxides of the preceding groups, whilst feeble basic properties only appear in the oxides RO_3 of the elements of the even series, and then only for those elements having a high atomic weight—that is, under those two conditions in which, as a rule, the basic characters increase. Even the lower types RO_2 and R_2O_3, &c., formed by the elements of group VI., are acid anhydrides in the uneven series, and only those of the elements of the even series have the properties of peroxides or even of bases.

Sulphur is the typical representative of group VI., both on account of the fact that the acid properties of the group are clearly defined in it and also because it is more widely distributed in nature than any of the other elements belonging to this group. Sulphur gives the typical compounds, H_2S, sulphuretted hydrogen, SO_3, sulphuric anhydride, and SO_2, sulphurous anhydride. And in all of them we find acid properties —SO_3 and SO_2 are anhydrides of acids, and H_2S is an acid, although a feeble one. As an element, sulphur has all the properties of a true non-metal; it has not a metallic lustre, does not conduct electricity, is a bad conductor of heat, is transparent, and combines directly with metals—in short, it has all the properties of the non-metals, like oxygen and chlorine. Furthermore, sulphur exhibits a distinct quantitative **resemblance to oxygen**, especially in the fact that, like oxygen, it combines **with two atoms of hydrogen**, and forms compounds resembling oxides with metals and non-metals. From this point of view sulphur is bivalent, if the halogens are univalent.[1] The chemical character of

---

[1] The individuality of sulphur is most clearly defined in its organo-metallic compounds. Not to dwell on this vast subject, which belongs to the province of organic chemistry, I think it not superfluous to compare the physical properties of the ethyl compounds of mercury, zinc, sulphur, and oxygen. The composition of all of them is expressed by the general formula $(C_2H_5)_2R$, where $R = Hg$, Zn, S, or O. They are all volatile: mercury ethyl, $Hg(C_2H_5)_2$, boils at 159°, its sp. gr. is 2·444, and its molecular volume, 106; zinc ethyl boils at 118°, has the sp. gr. 1·882, and the volume 101; ethyl sulphide, $S(C_2H_5)_2$, boils at 90°, has the sp. gr. 0·825, and the volume 107; common ether,

sulphur is clearly expressed by the fact that it forms a very slightly stable and feebly energetic acid with hydrogen. The salts corresponding with this acid are the sulphides, just as the oxides correspond to water and the chlorides to hydrochloric acid. However, as we shall afterwards see more fully, the sulphides are more closely analogous to the former than to the latter. But although combining with metals, as oxygen does, sulphur also forms chemically stable compounds with oxygen, and this fact impresses a peculiar character on all the relations of this element.[2]

Sulphur belongs to the number of those elements which **are very widely distributed in nature**, and it occurs both free and combined in various forms. The atmosphere, however, is almost entirely free from compounds of sulphur, although a certain amount of them should be present, if only from the fact that sulphurous anhydride is emitted from the earth in volcanic eruptions, and occurs in the air of cities, where much coal is burnt, since this always contains FeS_2. Sea and river water generally contain more or less sulphur in the form of sulphates. The beds of gypsum, sodium sulphate, magnesium sulphate, and the like are formations of undoubtedly aqueous origin. The sulphates contained in the soil are the source of the sulphur found in plants, and are indispensable to their growth. Among vegetable substances, the proteïds always contain from one to two per cent. of sulphur. From plants the albuminous substances, together with their sulphur, pass into the animal organism, and the decomposition of animal matter is accompanied by the odour of sulphuretted hydrogen as the product into which the sulphur passes in the decomposition of the albuminous substances. Thus, a rotten egg emits sulphuretted hydrogen. Sulphur occurs largely in nature, as the various insoluble sulphides of the metals. Iron, copper, zinc, lead, antimony, arsenic, &c., occur in nature combined with sulphur. These **metallic sulphides** frequently have a metallic lustre, and in the majority of cases occur

---

or ethyl oxide, $O(C_2H_5)_2$, boils at 35° has the sp. gr. 0·736, and the volume 101, in addition to which diethyl itself, $(C_2H_5)_2 = C_4H_{10}$, boils at about 0°, has a sp. gr. about 0·62, and a volume of about 94. Thus, the substitution of Hg, S, and O scarcely changes the volume, notwithstanding the difference of the weights; the physical influence, if one may so express oneself, of these elements, which are so very different in their atomic weights, is almost alike.

[2] Therefore Berzelius called sulphur an amphid element. Although the analogy between the compounds of sulphur and oxygen has been recognised from the very birth of modern chemistry (the oxides and sulphides are the most widely spread metallic ores in nature), still it has only been clearly expressed by the periodic system, which places both these elements in group VI. Here, moreover, stands out that parallelism which exists between SO_2 and ozone, OO_2, between K_2SO_3 and peroxide of potassium, K_2O_4 (Volkovitch in 1898 again drew attention to this parallelism).

crystallised, and also very often several sulphides occur combined or mixed together in these crystalline compounds. If they are yellow and have a metallic lustre they are called pyrites. Such are, for example, copper pyrites, $CuFeS_2$, and iron pyrites, FeS_2, which is the commonest of all. They are all also known as glances or blendes if they are greyish and have a metallic lustre—for example, zinc blende, lead glance, PbS, antimony glance, Sb_2S_3, &c. And, lastly, sulphur occurs **in the free state**. It occurs in this form in the most recent geological formations in admixture with limestone and gypsum, and most frequently in the vicinity of active or extinct volcanoes. As the gases of volcanoes contain sulphur compounds—namely, sulphuretted hydrogen and sulphurous anhydride, which by reacting on each other may produce sulphur, and as also the latter frequently appears in the craters of volcanoes as a sublimate—it might be imagined that the sulphur was of volcanic origin. But on a nearer acquaintance with its mode of occurrence, and more especially considering its relation to gypsum, $CaSO_4$, and limestone, the opinion most generally accepted at the present time is that the 'native' sulphur has been formed by the reduction of the gypsum by organic matter, and that its occurrence is only indirectly connected with volcanic agencies. Near Tetush, on the Volga, there are beds containing gypsum, sulphur, and asphalt (mineral tar). In Europe the most important deposits of sulphur are in the south of Sicily from Catania to Girgenti.[3] There are very rich deposits of sulphur in Daghestan, near Cherkai, and Cherkat in Khyut, near Mount Kanabour-bam, near Petrovsk, and in the Kira Koumski steppes in the transcaspian provinces, which are able to supply the whole of Russia with this mineral. Abundant deposits of sulphur have also been found in Kamtchatka in the neighbourhood of the volcanoes. The method of separation of the sulphur from its earthy impurities is based on the fact that sulphur melts when it is heated. The fusion is carried on at the expense of a portion of the sulphur, which is burnt, so that

---

[3] In Sicily I found, near Caltanisetta, a specimen of sulphur with mineral tar. In the same neighbourhood there are naphtha springs and mud volcanoes. It may be that these substances partly reduced the sulphur from gypsum.

The chief proof in favour of the origin of sulphur from gypsum is that in treating the deposits for the extraction of the sulphur it is found that the proportion of sulphur to calcium carbonate never exceeds that which it would be had they both been derived from calcium sulphate. As micro-organisms having the faculty of reducing and depositing sulphur from sulphates have been found in salt water, the origin of deposits of free sulphur in nature might be ascribed to their agency. Erenberg and others discovered micro-organisms (Beggiatoa, &c.) with granules of sulphur inside them many years ago, and Winogradsky demonstrated that they thrive in those localities where there is a supply of free sulphuretted hydrogen, from which they reduce the sulphur, which is then oxidised by the organisms to sulphuric acid.

the remainder may melt and run from the mass of the earth. This is carried on in special furnaces called *calcaroni*, built up of unhewn stone in the neighbourhood of the mines.[4]

Sulphur is purified by distillation in special retorts (see fig. 97) by passing the vapour into a chamber, G, built of stone. The first portions of the vapour entering the condensing chamber are condensed directly from the vapour into a solid state, and form a fine powder known as **flowers of sulphur.**[5] But when the temperature of the receiver attains the melting-point of sulphur, it passes into a liquid state and is cast into moulds (like sealing-wax), and is then known under the name of **roll sulphur.**[6]

In an uncombined state sulphur exists in **several modifications**, and forms a good example of the facility with which an alteration of properties can take place without a change of composition—that is, as regards the material of a substance. Common sulphur has the well-known yellow colour. This colour fades as the temperature falls, and

---

[4] Naturally only those ores of sulphur which contain a considerable amount of sulphur can be treated by this method. With poor ores it is necessary to have recourse to distillation or mechanical treatment in order to separate the sulphur; but its price is so low that this method in most cases is not profitable.

The sulphur obtained by the above-described method still contains some impurities, but it is frequently made use of in this form for many purposes, and especially in considerable quantities for the manufacture of sulphuric acid and for strewing over grapes. For other purposes, and especially in the preparation of gunpowder, a purer sulphur is required. Sulphur may be purified by distillation. The crude sulphur is called **rough,** and the distilled sulphur **refined.** The arrangement depicted in fig. 97 is employed for refining sulphur. The rough sulphur is melted in the boiler *d*, and as it melts it is run through the tube F into an iron retort, B, heated by the naked flame of the furnace. Here the sulphur is converted into vapour, which passes through a wide tube into the chamber G, surrounded by stone walls and furnished with a safety-valve, S.

[5] Flowers of sulphur always contain a certain amount of the oxides of sulphur.

[6] Sulphur may be extracted by various other means. It may be extracted from iron pyrites, FeS_2, which is very widely distributed in nature. From 100 parts of iron pyrites about half the sulphur contained, namely, about 25 parts, may be extracted by heating without access of air, a lower sulphide of iron, which is more stable under the action of heat, being left behind. Alkali waste (Chap. XII.), containing calcium sulphide and gypsum, $CaSO_4$, may be used for the same purpose; but native sulphur is so cheap that recourse can only be had to these sources when the calcium sulphide appears as a worthless by-product. The most simple process for the extraction of sulphur from alkali waste, in a chemical sense, consists in evolving sulphuretted hydrogen from the calcium sulphide by the action of hydrochloric acid. The sulphuretted hydrogen, when burnt, gives water and sulphurous anhydride, which reacts on fresh sulphuretted hydrogen with the separation of sulphur. The combustion of the sulphuretted hydrogen may be so conducted that a mixture of $2H_2S$ and SO_2 is straightway formed, and this mixture will deposit sulphur (Chap. XII., note 14). Gossage and Chance treat alkali waste with carbonic anhydride, and subject the sulphuretted hydrogen evolved to incomplete combustion (this is best done by passing a mixture of sulphuretted hydrogen and air, taken in the requisite proportions, over red-hot ferric oxide), by which means water and the vapour of sulphur are formed: $H_2S + O = H_2O + S$. As much as 80 per cent. of the sulphur contained in the soda refuse may be saved in this manner.

at −50° sulphur is almost colourless. It is very brittle, so that it may be easily converted into a powder, and it presents a crystalline structure, which, by the way, shows itself in the unequal expansion of lumps of sulphur by heat. Hence, when a piece of sulphur is heated by the warmth of the hand, it emits sounds, and sometimes cracks, which probably also depends on the bad heat-conducting power of this substance. It is easily obtained in a crystalline form by artificial means, because, although insoluble in water, it dissolves in carbon bisulphide and in certain oils.[7] Solutions of sulphur in carbon

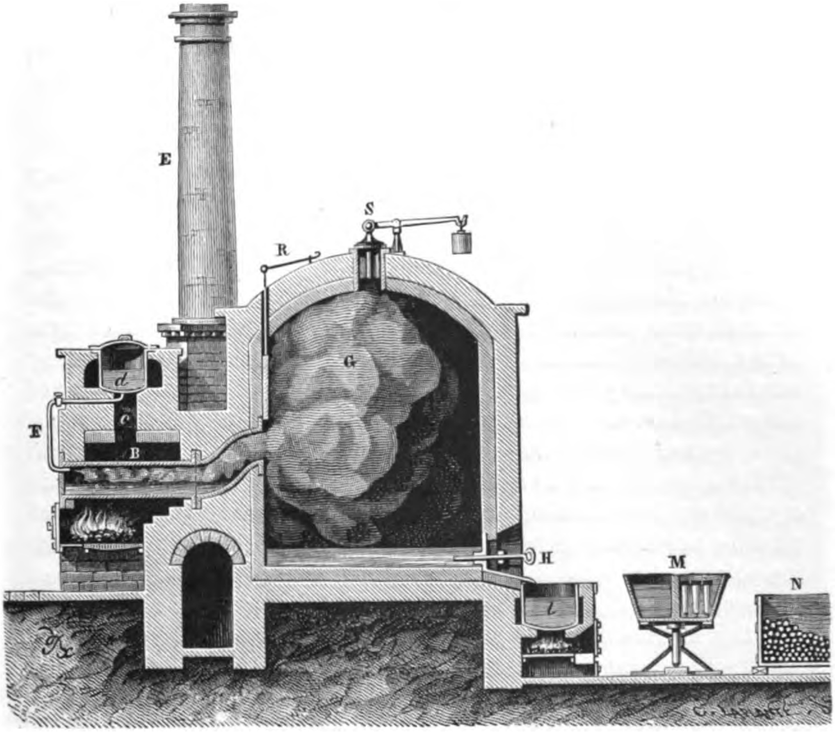


Fig. 97.—Refining sulphur by sublimation.

---

[7] One hundred parts of liquid carbon bisulphide, CS_2, dissolve 16·5 parts of sulphur at -11 , 24 parts at 0°, 37 parts at 15°, 46 parts at 22°, and 181 parts at 55°. The saturated solution boils at 55°, whilst pure carbon bisulphide boils at 47°. When sulphur is dissolved in carbon bisulphide it reduces the temperature, just as in the solution of salts in water. Thus, the solution of 20 parts of sulphur in 50 parts of carbon bisulphide at 22° lowers the temperature by 5°; 100 parts of benzene, C_6H_6, dissolve 0·965 part of sulphur at 26°, and 4·377 parts at 71°; chloroform, $CHCl_3$, dissolves 1·2 part of sulphur at 22°, and 16·85 parts at 174°.

bisulphide, when evaporated at the ordinary temperature, yield well-formed transparent crystals of sulphur in the form of **rhombic octahedra**, in which form it occurs native. The specific gravity of these crystals is 2·045. Fused sulphur, cast into moulds and cooled, has, after being kept a long time, a specific gravity 2·06, almost the same as that of the crystalline sulphur of the above form, which shows that common sulphur is the same as that which crystallises in octahedra. The specific heat of octahedral sulphur is 0·17 ; it melts at 114°, and forms a bright yellow mobile liquid. On further heating, the fused sulphur undergoes an alteration, which we shall presently describe, first observing that the above octahedral state of sulphur is its most stable form. At the ordinary temperature sulphur may be kept in this form for an indefinite length of time, and many other modifications of sulphur pass into this form after being left for a certain time at the ordinary temperature.

If sulphur is melted and then slightly cooled, so that it forms a crust on the surface and over the sides of the crucible, while the internal mass remains liquid, it then takes another crystalline form as it solidifies. This may be seen by breaking the crust and pouring out the remaining molten sulphur.[8] It is then found that the sides of the crucible are covered with oblique **prismatic crystals** of the monoclinic system ; they have an appearance totally different from that of the above-described crystals of rhombic sulphur. The prismatic crystals are brown, transparent, and less dense than the crystals of rhombic sulphur, their specific gravity being only 1·93, and their melting-point higher—about 119·3°.[8a] These crystals of sulphur cannot be kept at the ordinary temperature, which is indeed evident from the fact that in time they turn yellow ; the specific gravity also changes, and they pass completely into the ordinary modification. This transformation is accompanied by a considerable development of heat, so that the temperature of the mass may rise as much as 12°. Thus, **sulphur is dimorphous**—that is, it exists in two crystalline forms, and in the two forms it has independent physical properties. However, no chemical reactions are known which distinguish the two modifications

---

[8] Octahedral sulphur passes into the prismatic form at temperatures above 80°, as is seen from the fact that when a solution of sulphur in benzene is evaporated at temperatures higher than 80°, it leaves prismatic sulphur, while the same solution, evaporated at the ordinary temperature, deposits octahedral crystals. Also the octahedral crystals become opaque and form prismatic sulphur when heated to 90°. The latter is again transformed into octahedral sulphur at the ordinary temperature.

[8a] A. Smith and W. Holmes (1902) showed that the observed differences in the melting-point of sulphur are due to the presence of amorphous sulphur, which ordinary sulphur contains in variable proportions.

of sulphur, just as there are none distinguishing aragonite from calc spar.[9]

If molten sulphur is heated to 160°–220°, it loses its mobility and becomes thick and very dark-coloured, so that the crucible in which it is heated may be inverted without the sulphur running out. When heated above this temperature the sulphur again becomes more liquid, and at 250°–300° it is very mobile, although it does not acquire its original colour, and at 448° it boils. These modifications in the properties of sulphur depend not only on the variations of temperature, but also on a change of structure. If sulphur, heated to about 350°, is poured in a thin stream into cold water, it does not solidify into a solid mass, but retains its brown colour and **remains soft** ; it may be stretched out into threads, and is elastic, like gutta percha. But it does not remain in this soft and ductile state for a long time. After the lapse of a certain period the soft, transparent sulphur hardens, becomes opaque, passes into the ordinary yellow modification of sulphur, and in so doing develops heat, just as in the conversion of the prismatic into the octahedral variety. The soft sulphur is characterised by the fact that a certain portion of it is insoluble in carbon bisulphide. When soft sulphur is immersed in this liquid, only a portion of common sulphur passes into solution, whilst a certain portion is quite insoluble and remains so for a long time. The maximum proportion of insoluble sulphur is obtained by heating it slightly above 170°, especially in the presence of air, or when air, or SO_2 or HCl is passed through it;[9a] it lowers the fusing-point of sulphur. An exactly similar **insoluble (amorphous) sulphur** is obtained in certain reactions in the wet way, when sulphur separates out from solutions. Thus sodium thiosulphate, $Na_2S_2O_3$, when treated with acids, gives a

---

[9] If sulphur be cautiously melted in a U-tube immersed in a salt bath, and then gradually cooled, it is possible for all the sulphur to remain liquid at 100°. It will now be in a state of superfusion ; thus, by careful refrigeration, water may also be obtained in a liquid state at −10°, and a lump of ice then causes such water to form ice, and the temperature rises to 0 . If a prismatic crystal of sulphur be thrown into one branch of the U-tube containing the liquid sulphur at 100°, and an octahedral crystal be thrown into the other branch, then, as Gernez showed, the sulphur in each branch will crystallise in the corresponding form, and both forms are obtained at the same temperature; so that it is not the influence of temperature only which causes the molecules of sulphur to distribute themselves in one or another form, but also the influence of the crystalline parts already formed. This phenomenon is essentially analogous to that of supersaturated solutions.

[9a] A. Smith and W. Holmes (1902) found that 34–37 per cent. of amorphous sulphur are formed if these gases are passed into sulphur heated in its vapour (448°) for about 1½ hour. Not more than 5 per cent. are formed if the sulphur is heated in an atmosphere of NH_3, CO_2, H_2S, or N_2. Moreover, no amorphous sulphur at all is formed in NH_3; or, if it is formed, it is converted into the soluble variety. Smith and Holmes ascribe the molecule S_8 to amorphous sulphur.

precipitate of sulphur, which is insoluble in carbon bisulphide. The action of water on sulphur chloride also gives a similar modification of sulphur. Certain sulphides, when treated with nitric acid, also yield sulphur in this form.[10]

At temperatures of 448°–700° the vapour density of sulphur is 6·6 referred to air—i.e., about 96 referred to hydrogen.[10a] Hence at

---

[10] A certain amount of insoluble sulphur remains for a long time in the mass of soft sulphur, changing into the ordinary variety. Freshly cooled soft sulphur contains about one-third of insoluble sulphur, and after the lapse of two years it still contains about 15 per cent. Flowers of sulphur, obtained by the rapid condensation of sulphur from a state of vapour, also contains a certain amount of insoluble sulphur. *Rapidly distilled and condensed sulphur* also contains some insoluble sulphur. Hence a certain amount of insoluble sulphur is frequently found in roll sulphur. The action of light on a solution of sulphur converts a certain portion into the insoluble modification. Insoluble sulphur is of a lighter colour than the ordinary variety. It is best prepared by vaporising sulphur in a stream of carbonic anhydride, hydrochloric acid, &c., and collecting the vapour in cold water. When condensed in this manner it is nearly all insoluble in carbon bisulphide. It then has the form of hollow spheroids, and is therefore lighter than the common variety, having the sp. gr. 1·82. An idea of the modifications taking place in sulphur between 110° and 250° may be formed from the fact that at 150° liquid sulphur has a coefficient of expansion of about 0·0005, whilst between 150° and 250° it is less than 0·0003.

Engel (1891), by decomposing a saturated solution of hyposulphite of sodium (note 42) with HCl in the cold (the sulphur is not precipitated directly in this case), obtained, after shaking up with chloroform and evaporation, crystals of sulphur (sp. gr. 2·135), which, after several hours, passed into the insoluble (in CS_2) state, and in so doing became opaque and increased in volume. But if a mixture of solutions of $Na_2S_2O_3$ and HCl is allowed to stand, it deposits sulphur, which, after sufficient washing, is able to dissolve in water (like the colloidal varieties of the metallic sulphides, alumina, boron, and silver), but this colloidal *solution of sulphur* soon deposits sulphur insoluble in CS_2.

When a solution of sulphuretted hydrogen in water is decomposed by an electric current, the sulphur is deposited on the positive pole, and has therefore an electronegative character, and this sulphur is soluble in carbon bisulphide. When a solution of sulphurous acid is decomposed in the same manner, the sulphur is deposited on the negative pole, and is therefore electro-positive, and the sulphur so deposited is insoluble in carbon bisulphide. The sulphur which is combined with metals must have the properties of the sulphur contained in sulphuretted hydrogen, whilst the sulphur combined with chlorine is like that which is combined with oxygen in sulphurous anhydride. Hence Berthelot recognises the presence of soluble sulphur in metallic sulphides, and of the insoluble modification of amorphous sulphur in sulphur chloride. Cloëz showed that the sulphur precipitated from solutions is either soluble or insoluble, according to whether it separates from an alkaline or acid solution. If sulphur is melted with a small quantity of iodine or bromine, on pouring out the molten mass it forms amorphous sulphur, which keeps so for a very long time, and is insoluble, or nearly so, in carbon bisulphide. This is taken advantage of in casting certain articles in sulphur which by this means retain their tenacity for a long time; for example, the discs of electrical machines.

[10a] Bleyer and Cox determined the vapour density of sulphur under a low pressure, i.e., at lower temperatures, and found that it distinctly increases as the temperature falls, and gives reason for assuming that the molecule of sulphur contains 8 atoms (S_8) at low temperatures. This is all the more remarkable because the cryoscopic behaviour of solutions in benzene and molten naphthalene, according to Biltz and Herz, and the rise of boiling-point (in CS_2 by Beckmann and in CCl_4 by Oddo and Serra) both indicate that in

these temperatures **the molecule of sulphur contains six atoms** and has the composition S_6. The agreement between the observations of Dumas, Mitscherlich, Bineau, and Deville confirms the accuracy of this result. But in this respect the properties of sulphur were found to be variable. When heated to higher temperatures, that is to say, **above 800°**, the vapour density of sulphur is found to have one-third of this value, i.e., about 32 referred to hydrogen. At this temperature **the molecule of sulphur,** like that of hydrogen, oxygen, nitrogen, and chlorine, contains **only two atoms**; hence the molecular formula is then S_2. This variation in the vapour density of sulphur evidently corresponds with polymeric change, and may be likened to the transformation of ozone, O_3, into oxygen, O_2, or, better still, of benzene, C_6H_6, into acetylene, C_2H_2.[11]

In its faculty for combination, sulphur most closely resembles oxygen and chlorine; like them, it combines with nearly all the elements, with the development of heat and light, forming sulphur compounds, but as a rule this only takes place at a high temperature. At the ordinary temperature it does not enter into reactions, owing, with

---

solutions the molecule of sulphur contains 8 atoms. Hence the molecule of sulphur must now be considered to contain 8 atoms at low temperatures, 6 atoms at 400°–600° and only 2 atoms above 800°.

[11] Here, however, it is very important to remark that both benzene and acetylene can exist at the ordinary temperature, whilst the sulphur molecule S_2 only exists at high temperatures; and if this sulphur is allowed to cool, it passes first into S_6 and then into a liquid state, probably S_8, note 10a. Were it possible to have sulphur at the ordinary temperature in both the above modifications, in all probability the sulphur in the state S_2 would then present totally different properties from those which it has in the form S_6, just as the properties of gaseous acetylene are far from being similar to those of liquid benzene. Sulphur, in the form of S_2, is probably a substance which boils at a much lower temperature than the variety with which we are now dealing.

One must here call attention to the fact that sulphur, with all its analogy to oxygen (which also shows itself in its power to give the modification S_2), is also able to give a series of compounds containing more atoms of sulphur than the analogous oxygen compounds do of oxygen. Thus, for instance, compounds of five atoms of sulphur with 1 atom of barium, BaS_5, are known, whereas with oxygen only BaO_2 is known. On every side one cannot but see in sulphur a faculty for the union of a greater number of atoms than with oxygen. With oxygen the form of ozone, O_3, is very unstable, the stable form being O_2; whilst with sulphur, S_6 is the stable form and S_2 is exceedingly unstable. Furthermore, it is remarkable that sulphur gives a higher degree of oxidation, H_2SO_4, corresponding, as it were, with its complex composition, if we suppose that in S_6 four atoms of sulphur are replaced by oxygen and one by two atoms of hydrogen. The formulæ of its compounds, K_2SO_4, $K_2S_2O_3$, K_2S_5, BaS_5, and many others, have no analogues among the compounds of oxygen. They all correspond with the form S_6.

But although the form O_6 is unknown for oxygen, which only gives O_3, yet the tendency of oxygen to form complex compounds is seen in its capacity to give H_2O_2 and K_2O_4 (corresponds to Baeyer's ozonic acid and $= O_3 + K_2O$, that is, as it were, a hydrate of ozone), and in the power of the hydrogen compounds of the elements to form not only compounds with O_4 (Chap. XV.), but also the higher forms of peroxides. This apparently introduces a new form of analogy between sulphur and hydrogen.

other things, to the fact that it is a solid. In a molten state it acts on most metals and on the halogens. It burns in air at about 300°, and with carbon at a red heat, but it does not combine with nitrogen.

Fine wires, or the powders of the greater number of metals, burn in the vapour of sulphur. The direct combination of hydrogen with sulphur is restricted by a limit—that is, at a given temperature and under other given conditions it does not proceed unrestrictedly; there is no explosion or recalescence. Sulphuretted hydrogen, H_2S, decomposes at its temperature of formation—that is, it is easily dissociated.[12] The same phenomenon is repeated here as with water, except that the temperatures at which the attraction of hydrogen for sulphur begins and ceases are much lower than in the case of oxygen and hydrogen. The temperature at which combination takes place is here, as in many other instances, nearly the same as that at which dissociation begins. Hence **sulphuretted hydrogen** is formed in small quantity by the direct ignition of a mixture of the vapour of sulphur and hydrogen. However, the temperature must not be high, because otherwise the whole of the sulphuretted hydrogen will be decomposed; but at lower temperatures a small amount of sulphuretted hydrogen is formed by direct combination.[13] Sulphuretted hydrogen, however, like all other hydrogen compounds, may be easily obtained by the double decomposition of its corresponding metallic compounds, the replacement of the metal by hydrogen being effected by the action of acids on the sulphides according to the equation: $M_2S+H_2SO_4=H_2S+M_2SO_4$. However, it is not all sulphides or solutions of all acids that will evolve sulphuretted hydrogen, which fact is exceedingly characteristic, because, for example, all carbonates evolve carbonic anhydride when treated with any acid. Sulphuric acid will only evolve sulphuretted hydrogen from those sulphides which contain a metal capable of decomposing the acid with the evolution of hydrogen. Thus zinc, iron, calcium, magnesium, manganese, potassium, sodium, &c., form sulphides which evolve sulphuretted hydrogen when treated with sulphuric acid, and the metals themselves

---

[12] In the formation of potassium sulphide, K_2S (that is, in the combination of 32 parts of sulphur with 78 parts of potassium), about 100 thousand heat units are developed. Nearly as much heat is developed in the combination of an equivalent quantity of sodium; about 90,000 heat units in the formation of calcium or strontium sulphide; about 40,000 for zinc or cadmium sulphide, and about 20,000 for iron, cobalt, or nickel sulphide. Less heat is evolved in the combination of sulphur with copper, lead, and silver. According to Thomsen, H_2+S develops 4,512 calories.

[13] If sulphur is melted in a flask and heated nearly to its boiling-point, as Lidoff showed, the addition, drop by drop (from a funnel with a stopcock), of heavy (0·9) naphtha oil (of lubricating oleonaphtha), &c., is followed by a regular evolution of sulphuretted hydrogen. This is analogous to the action of bromine or iodine on paraffin and other oils, because hydrobromic or hydriodic acid is then formed (Chap. XI.). A certain amount of hydrogen sulphide is even formed when sulphur is boiled with water.

evolve hydrogen with acids.[14] The sulphides of those metals which do not liberate hydrogen from acids do not generally act on acids—that is, do not form sulphuretted hydrogen with them; such are, for example, the sulphides of lead, silver, copper, mercury, tin, &c. The usual mode of preparing sulphuretted hydrogen is by the action of **sulphuric acid on ferrous sulphide,** in which the same apparatus and method are employed as in the preparation of hydrogen, only replacing the metallic iron or zinc by ferrous sulphide. The reaction is expressed by the equation: $FeS + H_2SO_4 = FeSO_4 + H_2S$.[15]

In nature, sulphuretted hydrogen is formed in many ways. The

---

[14] However, the matter is really much more complicated. Thus zinc sulphide evolves sulphuretted hydrogen with sulphuric or hydrochloric acid, but does not react with acetic acid and is oxidised by nitric acid. Ferrous sulphide evolves sulphuretted hydrogen with acids, whilst the bisulphide, FeS_2, does not react with acids of ordinary strength. This absence of action depends, among other things, on the form in which the native iron pyrites occurs; it is a crystalline, compact, and very dense substance, and acids in general react with great difficulty on such metallic sulphides. This is seen very clearly in the case of zinc sulphide; if this substance is obtained by double decomposition, it separates as a white precipitate, which evolves sulphuretted hydrogen with great ease when treated with acids. Zinc sulphide is obtained in the same form when zinc is fused with sulphur, but native zinc sulphide—which occurs in compact masses of zinc blende and has a metallic lustre—is decomposed not at all or but slightly by sulphuric acid.

Another source of complication in the behaviour of the metallic sulphides towards acids depends on the action of water, and is shown by the fact that the action varies with different degrees of dilution or proportion of water present. The best known example of this is antimonious sulphide, Sb_2S_3, for strong hydrochloric acid, containing not more water than corresponds with $HCl,6H_2O$, decomposes even native antimony glance, with evolution of sulphuretted hydrogen, whilst dilute acid has no action, and in the presence of an excess of water the reaction, $2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$, occurs, whilst in the presence of a small amount of water the reaction proceeds in exactly the opposite direction. Here the participation of water in the reaction and its affinity are evident.

The facts that lead sulphide is insoluble in acids, that zinc sulphide is soluble in hydrochloric acid but insoluble in acetic acid, that calcium sulphide is even decomposed by carbonic acid, &c.—all these peculiarities of the sulphides are in correlation with the amount of heat evolved in the reaction of the oxides with hydrogen sulphide and with acids, as is seen from the observations of Favre and Silberman, and from the comparisons made by Berthelot in 1870.

[15] **Ferrous sulphide** is formed by heating a piece of iron to an incipient white heat, and then removing it from the furnace and bringing it into contact with a piece of sulphur. Combination then proceeds, accompanied by the development of heat, and the ferrous sulphide formed fuses. The sulphide of iron thus formed is a black, easily fusible substance, insoluble in water. When damp it attracts oxygen from the air, and is converted into green vitriol, $FeSO_4$. If all the iron does not combine with the sulphur in the method described above, the action of sulphuric acid will evolve hydrogen as well as hydrogen sulphide.

Ferrous sulphide may be advantageously replaced by calcium sulphide or a mixture of calcium and magnesium sulphides. A solution of magnesium hydrosulphide, MgS,H_2S, is very convenient, as at 60° it evolves a stream of pure hydrogen sulphide. A paste, consisting of CuS with crystals of $MgCl_2$ and water, may also be employed, since it only evolves H_2S when heated (Habermann).

most usual mode of its formation is by the decomposition of albuminous substances containing sulphur, as mentioned above. Another method is by the reducing action of organic matter on sulphates, and by the action of water and carbonic acid on the sulphides formed by this reduction. Volcanic eruptions are a third source of sulphuretted hydrogen in nature. Although sulphuretted hydrogen is formed in small quantities everywhere, it nevertheless soon disappears from the atmosphere, owing to its being easily decomposed by oxidising agencies. Many mineral waters contain sulphuretted hydrogen, and smell of it; they are called 'sulphur waters.'

Sulphuretted hydrogen, at the ordinary temperature, is a colourless gas, having a very unpleasant odour. It has, as its composition H_2S shows, a specific gravity seventeen times greater than that of hydrogen, and therefore it is somewhat heavier than air. Sulphuretted hydrogen **liquefies** at about —62°, or at the ordinary temperature when subjected to a pressure of 10 to 15 atmospheres; at —85° it is converted into a solid crystalline mass.[15a] One volume of water at 0° dissolves 4·37 volumes of sulphuretted hydrogen; at 10°, 3·58 volumes; and at 20°, 2·9 volumes.[16] The solutions impart a very feeble red coloration to litmus paper. This gas is poisonous. One part in fifteen hundred parts of air will kill birds. Mammalia die in an atmosphere containing $\frac{1}{200}$ part of this gas.

Sulphuretted hydrogen is very easily **decomposed** into its component parts by the action of heat or of a series of electric sparks.[16a] Hence it is not surprising that sulphuretted hydrogen undergoes change under the action of many substances having a considerable affinity for hydrogen and oxygen. Very many metals[17] evolve hydrogen with sulphuretted

---

[15a] Liquid sulphuretted hydrogen is most easily obtained by the decomposition of hydrogen polysulphide, which we shall presently describe, by the action of heat and in the presence of a small amount of water. If poured into a bent tube, like that described for the liquefaction of ammonia (Chap. VI.), the hydrogen polysulphide is decomposed by heat, in the presence of water, into sulphur and sulphuretted hydrogen, which condenses in the cold end of the tube into a colourless liquid.

[16] Sulphuretted hydrogen is still more soluble in alcohol than in water; one volume of the former at the ordinary temperature dissolves as much as eight volumes of the gas. The solutions in water and alcohol undergo change, especially in open vessels, owing to the fact that the water and alcohol dissolve oxygen from the atmosphere, which, acting on the sulphuretted hydrogen, forms water and sulphur. The solution may be so altered in this manner that every trace of sulphuretted hydrogen disappears. Solutions of sulphuretted hydrogen in glycerine change much more slowly, and may therefore be kept for a long time as reagents. De Forcrand obtained a hydrate, $H_2S,16H_2O$, resembling the hydrates given by many other gases.

[16a] Hautefeuille observed not only the formation of H_2S from sulphur and hydrogen, but also the decomposition of H_2S at 400°, and Konovaloff observed the formation at 310°, but decomposition did not take place at that temperature.

[17] Some metals evolve hydrogen from sulphuretted hydrogen at the ordinary tem-

hydrogen, so that in this respect it presents the property of an acid; for instance, $2H_2S+Sn=2H_2+SnS_2$. This may be taken advantage of for determining the composition of sulphuretted hydrogen, because a given volume then leaves the same volume of hydrogen. On the other hand, oxygen,[18] chlorine,[19] or even iodine decomposes sulphuretted hydrogen, removing the hydrogen from it and leaving free sulphur, so that in this reaction the sulphur is replaced by the above-named elements; for example, $H_2S+Br_2=2HBr+S$. In no other hydrogen compound is it so easy to show the **substitution**, both of hydrogen and of the element combined with it, as in hydrogen sulphide. This clearly proves the feeble union between the elements forming this gas. Oxidising agents accomplish the separation of the sulphur very easily; for instance, nitrous acid, chromic acid, and even ferric oxide and the higher oxides like it. Thus, if sulphuretted hydrogen is passed into a solution of chromic acid or an acid solution of ferric oxide, water is formed, **and the sulphur is separated in a free state.** Thus, sulphuretted hydrogen acts as a **reducing agent** in virtue of the hydrogen it contains. In the presence of an excess of a powerful oxidising agent a portion of the sulphur may also be oxidised and form sulphuric acid. The reducing action of sulphuretted hydrogen is frequently applied in chemical manipulations for the preparation of lower oxides and for the conversion of certain oxygen compounds into hydrogen compounds; the higher oxides of nitrogen are converted into ammonia, and in the presence of alkalies the nitro-compounds are converted into ammonia derivatives, &c. The action of sulphuretted hydrogen on sulphurous anhydride belongs to this class of phenomena, the chief products being sulphur and water, $2H_2S+SO_2=2H_2O+S_3$.

The acid character of sulphuretted hydrogen is clearly seen in its action on alkalies and salts.[19a] Thus, lead oxide and its salts, in the presence of sulphuretted hydrogen, form water or an acid, and sulphide of lead: $PbX_2+H_2S=PbS+2HX$. This reaction takes place

---

perature. For example, the light metals, and copper and silver (especially with access of air?) among the heavy metals. Hence articles made of silver turn black in the presence of vapours containing sulphuretted hydrogen, because silver sulphide is black. Zinc and cadmium act at a red heat, but not completely.

[18] If sulphuretted hydrogen escapes from a fine orifice into the air, it will burn when lighted, and will be transformed into sulphurous anhydride and water. But if it burns in a limited supply of air—for instance, when a cylinder is filled with it and lighted—then only the hydrogen burns, which has, judging from the amount of heat developed in its combustion and from all its properties, a greater affinity for oxygen than sulphur. In this respect the combustion of sulphuretted hydrogen resembles that of hydrocarbons.

[19] Hence bleaching powder and chlorine destroy the disagreeable smell of sulphuretted hydrogen. (For the reaction of hydrogen sulphide and iodine, see Chap. XI.)

[19a] Perfectly dry H_2S (Hughes, 1892) has no action upon perfectly dry salts, just as dry HCl does not react with dry NH_3 or metals (Chap. IX., note 29).

even in the presence of powerful acids, because lead sulphide is one of those sulphides which are unacted on by acids, and in solutions the reaction is a complete one. This reaction is taken advantage of for the preparation of many acids, by first converting into a lead salt, and then submitting this salt to the action of sulphuretted hydrogen. For example, lead formate with sulphuretted hydrogen gives formic acid. Sulphuretted hydrogen in acting on a number of metallic acid substances in solution or in an anhydrous state also forms corresponding sulphates: (1) if it does not reduce the acid; (2) if the sulphur compound corresponding with the anhydride of the acid is insoluble in water, the reaction proceeds in solutions; (3) if the sulphuretted hydrogen and the acid taken do not come into contact with an alkali, on which they would be able to act first; and (4) if the sulphur compound is not decomposed by water. Thus, solutions of arsenious acid give a precipitate of arsenious sulphide, As_2S_3, with sulphuretted hydrogen. This reaction proceeds in the presence not only of water, but also of acids, because the latter do not decompose the resultant sulphur compounds. The type of the decomposition is the same as with bases—that is, the sulphur and oxygen change places: $RO_n + nH_2S = RS_n + nH_2O$. Some sulphides corresponding with acid anhydrides are decomposed by water, and therefore are not formed in the presence of water. Such, for example, are the sulphides of phosphorus.[20]

---

[20] The sulphide P_4S is obtained by cautiously fusing the requisite proportions of common phosphorus and sulphur under water; it is a liquid which solidifies at 0°, and may be distilled without undergoing change, but it fumes in air and easily takes fire. The higher sulphide, P_2S, has similar properties. But little heat is evolved in the formation of these compounds, and it may be supposed that they are formed by the direct conjunction of whole molecules of phosphorus and sulphur; but if the proportion of sulphur be increased, the reaction is accompanied by so considerable a rise of temperature that an explosion takes place, and for the sake of safety red phosphorus must be used, mixed as intimately as possible with powdered sulphur and heated in an atmosphere of carbonic anhydride. The higher compounds are decomposed by water. By increasing the proportion of sulphur, the following compounds have been obtained: P_4S_3 as prisms (fusing at 165°, Rebs), soluble in carbon bisulphide, and unaltered by air and water; **phosphorus trisulphide**, P_2S_3, the analogue of P_2O_3, is a light-yellow crystalline compound only slightly soluble in carbon bisulphide; it is fusible and volatile, is decomposed into hydrogen sulphide and phosphorous acid by water, and, like the highest compound of sulphur and phosphorus, P_2S_5, forms thio-salts with potassium sulphide, &c. This **phosphorus pentasulphide** corresponds with phosphoric anhydride; like the trisulphide, it gives hydrogen sulphide and phosphoric acid with an excess of water. It reacts in many respects like phosphoric chloride. The sulphide PS_2 is also known; the vapour density of this compound seems to indicate a molecule, P_3S_6.

Phosphorus sulphochloride, $PSCl_3$, corresponds with phosphorus oxychloride It is a colourless, pleasant-smelling liquid, boiling at 124°, and of sp. gr. 1·63; it fumes in air and is decomposed by water: $PSCl_3 + 4H_2O = PH_3O_4 + H_2S + 3HCl$. It is obtained when phosphoric chloride is treated with hydrogen sulphide, hydrochloric acid being also formed; it is also produced by the action of phosphoric chloride on certain sulphides—for example, on antimonious sulphide, also by the (cautious) action of phosphorus on sulphur

The metallic sulphides corresponding with the metallic oxides have either a feeble alkaline or a feeble acid character, according to the character of the corresponding oxide, and therefore by combining together they are able to form saline substances—that is, salts in which the oxygen is replaced by sulphur. Thus sulphuretted hydrogen, having the properties of a feeble acid,[21] has, at the same time, the properties of water, and forms the type of the sulphurous or thio-derivatives, which may also be formed by means of sulphuretted hydrogen, just as the oxides may be formed by the aid of water. But as sulphuretted hydrogen has acid properties, it combines more easily with the basic metallic sulphides. Hence, for instance, there exists a compound of sulphuretted hydrogen with potassium sulphide, potassium hydrosulphide, $2KHS = K_2S + H_2S$, just as there are potassium hydroxides; but there are scarcely any compounds of sulphuretted hydrogen with the sulphides corresponding with acids. Thus the sulphides of the metals may be regarded either as salts of sulphuretted hydrogen or as oxides of the metals in which the oxygen is replaced by sulphur. In general terms, the sulphides exhibit the same degrees of difference with respect to their solubility in water as do the oxides. Thus, the oxides of the alkali metals and of some of the metals of the alkaline earths, are soluble in water, whilst those of nearly all the other metals are insoluble. Those metals, like aluminium, whose oxides—for example, Al_2O_3—have intermediate properties and do not form compounds with feeble acids, at least in a wet way, also do not form sulphides by this method, although these may be obtained indirectly. And in general the sulphides of the metals are easily formed in a wet way, and with particular ease if they are insoluble in water. In this case their salts enter into double decomposition with

---

chloride: $2P + 3S_2Cl_2 = 2PSCl_3 + 4S$; by the action of PCl_5 upon certain sulphides, for example, Sb_2S_3; by the reaction: $3MCl + P_2S_5 = PSCl_3 + M_3PS_4$ (Glatzel, 1893), and in the reaction, $3PCl_3 + SOCl_2 = PCl_5 + POCl_3 + PSCl_3$, showing the reducing action of phosphorus trichloride, which is especially clear in the reaction, $SO_3 + PCl_3 = SO_2 + POCl_3$. Thorpe and Rodger (1889), by heating $3PbF_2$ or BiF_3 with phosphorus pentasulphide (and also by heating AsF_3 and $PSCl_3$ to 150°), obtained thiophosphoryl fluoride as a colourless, spontaneously inflammable gas (see further on, note 74a, and Chap. XIX. note 25). The action of $PSCl_3$ upon NaHO gives a salt of *monothiophosphoric acid* (Würtz, Kubierschky), H_3PSO_3, which yields soluble salts with alkalies.

[21] Sulphuretted hydrogen does not saturate the alkaline properties of alkali hydroxides, so that a solution of potassium hydroxide will not under any circumstances give a neutral liquid with sulphuretted hydrogen. Sulphuretted hydrogen forms in solution only an acid salt with the potassium: $KHO + H_2S = KHS + H_2O$, but not K_2S. Furthermore, it must be taken into account that potassium oxide, K_2O, and the anhydrous oxides like it, do not exist in solutions, for whenever they are formed they immediately react with the water, forming caustic potash, KHO, &c. In the same way, directly potassium sulphide, K_2S, is formed in water it is decomposed into potassium hydroxide and hydrosulphide: $K_2S + H_2O = KHO + KHS$ (see note 27).

sulphuretted hydrogen, or with soluble sulphides, and give an insoluble sulphide—for instance, a salt of lead gives lead sulphide with sulphuretted hydrogen. By the action of sulphuretted hydrogen on a salt of a metal, a free acid must be formed besides the metallic sulphide. Thus if a metal M be in a state of combination MX_2, then by the action of sulphuretted hydrogen there will be formed, besides MS,[22] an acid 2HX. It is evident that sulphuretted hydrogen will not precipitate an insoluble sulphide from the salts of those metals whose sulphides react with free acid, such as zinc, iron, manganese, &c. The reaction, $FeCl_2+H_2S=FeS+2HCl$, and the like, do not take place, because the acid acts on the ferrous sulphide. Antimonious sulphide is not acted on by dilute hydrochloric acid, but it is decomposed by strong acid, and therefore, in presence of an excess of hydrochloric acid, antimonious chloride does not entirely react with hydrogen sulphide, whilst the reaction, $2SbCl_3+3H_2S=Sb_2S_3+6HCl$, is a complete one in a dilute solution and with a small quantity of acid. Those metallic sulphides which are decomposed by acids may be obtained in a wet way by the double decomposition of the salts of the metals, not with hydrogen sulphide, but with soluble metallic sulphides, such as sulphide of ammonium or of potassium, because then no free acid is formed, but a salt of the metal (potassium or ammonium) which was taken as a soluble sulphide. Thus, for example, $FeCl_2+K_2S=FeS+2KCl$.[23]

---

[22] During recent years (beginning with Schulze, 1882) it has been found that many metallic sulphides which were considered totally insoluble do, under certain circumstances, form very unstable solutions in water, as already mentioned in Chap. I., note 57. Arsenic sulphide is very easily obtained in the form of a solution (hydrosol). Solutions of copper and cadmium sulphides may also be easily obtained by precipitating their salts, CuX_2, or CdX_2, with ammonium sulphide and washing the precipitate; but they are reprecipitated by the addition of foreign salts.

[23] In reality the preceding reaction should be expressed thus: $FeCl_2+2KHS=FeS+2KCl+H_2S$ (note 21), because in the presence of water not K_2S but KHS reacts. But as the sulphuretted hydrogen takes no part in the reaction, it is usual to express the formation of such sulphides without taking the hydrogen sulphide proceeding from the potassium or ammonium hydrosulphides into account. It is not usual to employ potassium sulphide but ammonium sulphide—or, to speak more accurately, ammonium hydrosulphide—in order to avoid the formation of a non-volatile salt of potassium and to have, together with the sulphide formed, a salt of ammonium which can always be driven off by evaporating the solution and igniting the residue. Thus the metallic sulphides may be divided into three chief classes: (1) **those soluble in water,** (2) **those insoluble in water but reacting with acids,** and (3) **those insoluble in both water and acids.** The third class may be easily subdivided into two groups; to the first group belong those sulphides which correspond with bases or basic oxides, and are therefore unable to play the part of an acid with the sulphides of the alkalies, and are insoluble in NH_4HS, whilst the sulphides of the second group are of an acid character, and give soluble thio-salts with the sulphides of the alkaline metals, in which they play the part of an acid. To this group belong those metals whose corresponding oxides have acid properties. It must be observed, however, that not all metallic acids have corresponding sulphides, partly owing to the fact that certain acids are reducible by sulphuretted hydrogen, especially

Metallic sulphides may be obtained by many other means besides the action of sulphuretted hydrogen on salts and oxides, or by the simple combination of metals with sulphur when heated or fused. Thus, they may also be formed by the reduction of sulphates either by heating them with charcoal or by other means. Charcoal takes up the oxygen from many sulphates, leaving corresponding sulphides. Thus sodium sulphate, Na_2SO_4, when heated with charcoal, forms sodium sulphide, Na_2S. Besides which, metallic sulphides are also obtained by heating metals or their oxides in the vapours of many sulphur compounds—for example, in the vapour of carbon bisulphide, CS_2, when the carbon takes up the oxygen and the sulphur combines with the

---

when their lower degrees of oxidation are of a basic character. Such are, for instance, the acids of chromium, manganese, &c. Sulphuretted hydrogen converts them into lower oxides, having the properties of bases. Those bases which do not combine with feeble acids, such as carbonic acid and hydrogen sulphide, give a precipitate of hydroxide with ammonium sulphide; for example, aluminium salts react in this manner. This difference of the metals in their behaviour towards sulphuretted hydrogen gives a very valuable means of separating them from each other, and **is taken advantage of in analytical chemistry**. If, for instance, the metals of the first and third groups occur together, it is only necessary to convert them into soluble salts, and to act on the solution of the salts with sulphuretted hydrogen; this will precipitate the metals of the third group in the form of sulphides, whilst the metals of the first group will not be in the least acted on. Such a method of separating the metals is considered more fully in analytical chemistry, and we shall therefore limit ourselves here to pointing out to which groups the most common metals belong, and the colour which is proper to the sulphide precipitated.

Metals which are precipitated by sulphuretted hydrogen, as sulphides from a solution of their salts, even in the presence of free acid:

The precipitate is soluble in ammonium sulphide:

Platinum (dark brown)
Gold (dark brown)
Tin (yellow and brown)
Antimony (orange)
Arsenic (yellow)

The precipitate is insoluble in ammonium sulphide:

Copper (black)
Silver (black)
Cadmium (yellow)
Mercury (black)
Lead (black)

Metals which are precipitated by ammonium sulphide from neutral solutions, but not precipitated from acid solutions by sulphuretted hydrogen:

The sulphide precipitated is soluble in hydrochloric acid:

Zinc (white) | *Manganese* (rose colour) | *Iron* (black)

The sulphide precipitated is not soluble in dilute hydrochloric acid:

Nickel (black) | *Cobalt* (black)

A hydroxide, and not a sulphide, is precipitated:

Chromium (green) | *Aluminium* (white)

The metals of the alkalies and of the alkaline earths are not precipitated by either sulphuretted hydrogen or ammonium sulphide. The metals of the alkaline earths when in acid solutions in the form of phosphates and many other salts are precipitated by ammonium sulphide, because the latter neutralises the free acid, with formation of an ammonium salt of the acid and evolution of sulphuretted hydrogen.

metal. The sulphides formed in this manner are often crystalline, and often appear with those properties and in that crystalline form in which they occur in nature. Besides which, we must mention that many of the sulphides of the metals are oxidised in air at the ordinary, and especially at a higher, temperature, forming either SO_2 and the oxide of the metal or sulphates. This oxidation preceeds with particular ease, even at the ordinary temperature, when a metallic sulphide is precipitated from its solutions as a fine powder containing water. The sulphides of iron and manganese, &c., are very easily oxidised in this manner. But if these hydrates are ignited, they lose their water (the ignition must be carried on in a stream of hydrogen to prevent their oxidation during the process), become denser, and are no longer oxidised at the ordinary temperature. Those sulphides whose corresponding sulphates are decomposed by heat part with their sulphur in the form of sulphurous anhydride when they are ignited in air, and the metal, as a rule, remains behind as oxide. This is taken advantage of in the treatment of sulphurous ores. The process is called **roasting**.

Hydrogen not only forms sulphuretted hydrogen with sulphur, but also combines with it in several other proportions, just as it does with oxygen, forming not only water but also hydrogen peroxide. Moreover, these **polysulphides of hydrogen** are unstable, like hydrogen peroxide, and are also obtained from the corresponding polysulphides of the metals of the alkaline earths, just as hydrogen peroxide is obtained from barium peroxide. Thus, calcium forms not only calcium sulphide, CaS, but also bi-, tri-, and penta-sulphides, CaS_5, and all these compounds are soluble in water. Sodium also forms sulphides from Na_2S to Na_2S_5. If an acid is added to a solution of a polysulphide, it gives sulphur, sulphuretted hydrogen, and a salt of the metal. For instance, $MS_5+2HCl=MCl_2+H_2S+4S$. If we reverse the operation, and pour a solution of a polysulphide into an acid, sulphur is not precipitated, but an oily liquid is formed which is heavier than water and insoluble in it. This is the polysulphide of hydrogen : $MS_5+2HCl=MCl_2+H_2S_5$. As was shown by Rebs (1888), whatever polysulphide of sodium is taken, it always gives one and the same **hydrogen pentasulphide**[24] of specific gravity 1·71 (15°). It can only

---

[24] Rebs took di-, tri-, tetra-, and penta-sulphides of sodium, potassium, and barium, which he prepared by dissolving sulphur in solutions of the normal sulphides; on adding hydrochloric acid he always obtained hydrogen pentasulphide, whence it is evident that $4H_2S_n=(n-1)H_2S_5+(5-n)H_2S$. For example, if H_2S_2 were formed, it would decompose according to the equation, $4H_2S_2=H_2S_5+3H_2S$. The hydrogen pentasulphide formed breaks up into hydrogen sulphide and sulphur when brought into contact with water. Previous to Rebs's researches many chemists stated that all polysulphides gave the bisulphide H_2S_2, and Hofmann recognised only hydrogen trisulphide, H_2S_3.

be preserved in the absence of water and at low temperatures, and then not for long: for, especially in the presence of alkalies and when slightly warmed, it splits up very easily into sulphuretted hydrogen and sulphur.[25]

The soluble sulphides and polysulphides of the metals of the alkalies and alkaline earths — for example, of ammonium,[26]

---

[25] The formation of the polysulphides of hydrogen, H_2S_n, is easily understood, like that of the saturated hydrocarbons, C_nH_{2n+2}, from the law of substitution, knowing that sulphur gives H_2S, because the molecule of sulphuretted hydrogen may be divided into H and HS. This radicle HS is equivalent to H. By substituting this radicle for hydrogen in H_2S we obtain $(HS)HS = H_2S_2$, $(HS)(HS)S = H_2S_3$, &c., so that the compounds represented by H_2S_n forms homologues of H_2S. The question arises why in H_2S_n the apparent limit of n is 5—that is, why does the substitution end with the formation of H_2S_5? The answer appears to me to be clearly because in the molecule of sulphur, S_6, there are six atoms of sulphur (note 11). The forces in the one and the other case are the same. In the one case they hold S_6 together, in the other S_5 and H_2; and, judging from H_2S, the two atoms of hydrogen are equal in power and significance to the atom of sulphur. Just as hydrogen peroxide, H_2O_2, expresses the composition of ozone, O_3, in which O is replaced by H_2, so also H_2S_5 corresponds with S_6.

[26] **Ammonium sulphide**, $(NH_4)_2S$, may be prepared by passing sulphuretted hydrogen into a vessel full of dry ammonia, or by passing the two dry gases together into a very cold receiver. In the latter case it is necessary to prevent the access of air, and to have an excess of ammonia. Under these circumstances, two volumes of ammonia combine with one volume of sulphuretted hydrogen, and form a colourless, very volatile, crystalline substance, which has an unpleasant odour, and is very poisonous and exceedingly unstable. When exposed to the air it absorbs oxygen and acquires a yellow colour, and then contains oxygen and polysulphide compounds (because a portion of the hydrogen sulphide gives water and sulphur). It is soluble in water and forms a colourless solution, which, however, in all probability contains free ammonia and the acid salt—that is, ammonium hydrosulphide, NH_4HS, or $(NH_4)_2S,H_2S$. This salt is formed when dry ammonia is mixed with an excess of dry sulphuretted hydrogen. The compound contains equal volumes of the components, $NH_3 + H_2S = (NH_4)HS$. It crystallises in an anhydrous state in colourless plates, and may be easily volatilised (dissociating, like ammonium chloride), even at the ordinary temperature; it has an alkaline reaction, absorbs oxygen from the air, is soluble in water, and its solution is usually prepared by saturating an aqueous solution of ammonia with sulphuretted hydrogen.

A solution of ammonium sulphide is able to dissolve sulphur, and then contains compounds of hydrogen polysulphide and ammonia. Some of these compounds may be obtained in a crystalline form. Thus Fritzsche obtained a compound of ammonia with hydrogen pentasulphide, or **ammonium pentasulphide**, $(NH_4)_2S_5$, in the following manner: He saturated an aqueous solution of ammonia with sulphuretted hydrogen, added powdered sulphur to it, and passed ammonia gas into the solution, which then absorbed a fresh amount. After this he again passed sulphuretted hydrogen into the solution and then added sulphur, and then again ammonia. After repeating this several times, orange-yellow crystals of $(NH_4)_2S_5$ separated out from the liquid. These crystals melted at 40° to 50°, and were very unstable.

When a solution of ammonium hydrosulphide, prepared by saturating a solution of ammonia with sulphuretted hydrogen, is exposed to the air, it turns yellow, owing to the presence of an ammonium polysulphide, whose formation is due to the sulphuretted hydrogen being oxidised by the air and converted into water and sulphur, which is dissolved by the ammonium sulphide. In certain analytical reactions it is usual to employ a solution of ammonium sulphide which has been kept for some time and has acquired a yellow colour. This yellow sulphide of ammonium deposits sulphur when saturated with potassium,[27] and calcium [28]—have the appearance and properties of salts,

---

acids, whilst a freshly prepared solution only evolves sulphuretted hydrogen. The yellow solution furthermore contains ammonium thiosulphate, which is derived not only from the oxidation of the ammonium sulphide, but also from the action of the liberated sulphur on the ammonia, just as an alkaline salt of thiosulphuric acid and a sulphide are formed by the action of sulphur on a solution of a caustic alkali.

[27] **Potassium sulphide**, K_2S, is obtained by heating a mixture of potassium sulphate and charcoal to a red heat. It may be prepared in solution by taking a solution of potassium hydroxide, dividing it into two equal parts, and saturating one portion with sulphuretted hydrogen so long as it is absorbed. This portion will then contain the acid salt, KHS (note 21). The two portions are then mixed together, when potassium sulphide is obtained in the solution. This solution has a strongly alkaline reaction, and is colourless when freshly prepared, but it very easily undergoes change when exposed to the air, forming potassium thiosulphate and polysulphides. When the solution is evaporated at low temperatures under the receiver of an air-pump, it yields crystals of the composition $K_2S,5H_2O$ (heated at 150°, they part with 3 mol. H_2O, and at higher temperatures they lose nearly all their water without evolving sulphuretted hydrogen). When they are ignited in glass vessels they corrode the glass. When a solution of caustic potash, completely saturated with sulphuretted hydrogen, is evaporated under the receiver of an air-pump, it forms colourless rhombohedra of hydrated **potassium hydrosulphide**, $2(KHS),H_2O$ (Schöne). These crystals are deliquescent in the air, but do not change in a vacuum when heated up to 170°, and at higher temperatures they lose water but do not evolve sulphuretted hydrogen. The anhydrous compound, KHS, fuses at a dark-red heat into a very mobile yellow liquid, which gradually becomes darker in colour and solidifies to a red mass. It is remarkable that when a solution of the compound KHS is boiled it somewhat easily evolves half its sulphuretted hydrogen, leaving potassium sulphide, K_2S, in solution; and a solution of the latter in water is also able to evolve sulphuretted hydrogen on prolonged boiling, but the evolution cannot be rendered complete, so that at a certain temperature a solution of potassium sulphide will not be capable of absorbing sulphuretted hydrogen at all. From this we must conclude that potassium hydroxide, water, and sulphuretted hydrogen form a system whose complex equilibrium is subject to the laws of dissociation and depends on the relative mass of each substance, on the temperature, and on the dissociation pressures of the component elements. Potassium sulphide is soluble not only in water, but also in alcohol.

Berzelius showed that in addition to potassium sulphide there also exist potassium bisulphide, K_2S_2; trisulphide, K_2S_3; tetrasulphide, K_2S_4; and pentasulphide, K_2S_5. According to the researches of Schöne, the last three are the most stable. These different compounds of potassium and sulphur may be prepared by fusing potassium hydroxide or carbonate with an excess of sulphur in a porcelain crucible in a stream of carbonic anhydride. At about 600° potassium pentasulphide is formed. When heated to 800° it loses one-fifth of its sulphur and gives the tetrasulphide, which at this temperature is stable. At a bright-red heat—namely, about 900°—the trisulphide is formed. This compound may also be formed by igniting potassium carbonate in a stream of carbon bisulphide, in which case a compound, K_2CS_3, corresponding to potassium carbonate, is first formed and carbonic anhydride evolved. On further ignition, this compound splits up into carbon and potassium trisulphide, K_2S_3. The tetrasulphide may also be obtained in solution if a solution of potassium sulphide be boiled with the requisite amount of sulphur without access of air. This solution yields red crystals of the composition $K_2S_4,2H_2O$ when it is evaporated in a vacuum. These crystals are very hygroscopic, easily soluble in water, but very sparingly so in alcohol; when ignited they give off water, sulphuretted hydrogen, and sulphur. If a solution of potassium sulphide is boiled with an excess of sulphur it forms the pentasulphide, which is, however, decomposed on prolonged boiling into sulphuretted hydrogen and potassium thiosul-

[28] See p. 247.

whilst the sulphides of the heavy metals resemble their oxides and have

---

phate: $K_2S_5 + 3H_2O = K_2S_2O_3 + 3H_2S$. A substance called **liver of sulphur** was formerly frequently used in chemistry and medicine. Under this name is known the substance which is formed by boiling a solution of caustic potash with an excess of flowers of sulphur. This solution contains a mixture of potassium pentasulphide and thiosulphate, $6KHO + 12S = 2K_2S_5 + K_2S_2O_3 + 3H_2O$. The substance obtained by fusing potassium carbonate with an excess of sulphur was also known as liver of sulphur. The sulphides of sodium, for example, Na_2S, $NaHS$, &c., in many respects closely resemble the corresponding potassium compounds.

[28] The metals of the alkaline earths, like those of the alkalies, form several compounds with sulphur; thus calcium forms compounds with one and with five atoms of sulphur. There are doubtless also intermediate sulphides. If sulphuretted hydrogen is passed over ignited lime, it forms water and **calcium sulphide**, which may also be formed by heating calcium sulphate with charcoal, whilst if sulphur is heated with lime or with calcium carbonate, oxygen compounds (calcium thiosulphate and sulphate) are naturally formed at the same time as calcium sulphide. The prolonged action of the vapour of carbon bisulphide, especially when mixed with carbonic anhydride, on strongly ignited calcium carbonate converts it completely into sulphide. Calcium sulphide is generally obtained as an almost colourless, opaque, brittle mass, which is infusible at a white heat, and is soluble in water. The act of solution (as with K_2S, note 22) is partly accompanied by a double decomposition with the water. When heated, dry calcium sulphide does not absorb oxygen from the air. An excess of water decomposes it, like many other metallic sulphides, precipitating lime (as a product of the decomposition the lime hinders the action of the water upon the CaS; see soda refuse, Chap. XII., note 12), and forming a hydrosulphide, CaH_2S_2, in solution. This compound is also formed by passing sulphuretted hydrogen through an aqueous solution of calcium sulphide or lime. Its solution has an alkaline reaction. It decomposes when evaporated, and absorbs oxygen from the air. **Calcium pentasulphide**, CaS_5, is not known in a pure state, but may be obtained in admixture with calcium thiosulphate by boiling a solution of lime or calcium sulphide with sulphur: $3CaH_2O_2 + 12S = 2CaS_5 + CaS_2O_3 + 3H_2O$. A similar compound in an impure form is formed by the action of air on alkali waste, and is used for the preparation of thiosulphates.

Many of the sulphides of the metals of the alkaline earths are phosphorescent—that is, they have the faculty of **emitting light in the dark**, after having been subjected to the action either of sunlight or of any bright source of light. The luminosity lasts some time, but is not permanent and gradually disappears. This phosphorescent property is inherent, in a greater or less degree, to nearly all substances (Becquerel), but for a very short time; whilst with calcium sulphide it is comparatively durable, lasting for several hours, and Dewar (1894) showed that it is far more intense at very low temperatures (for instance, in bodies cooled in liquid oxygen to $-182°$). It is due to the excitation of the surfaces of substances by the action of light, and is determined by those rays which exhibit a chemical action. Hence daylight or the light of burning magnesium acts more powerfully than the light of a lamp. According to the observations of Becquerel, the presence of compounds of manganese, bismuth, sodium sulphide (but not potassium sulphide), &c., although in minute traces, is absolutely indispensable. This gives reason for thinking that the formation and decomposition of double salts perhaps form the chemical cause of the phenomena. Compounds of strontium and barium have this property to an even greater extent than calcium sulphide. These compounds may be prepared as in the following example: A mixture of sodium thiosulphate and strontium chloride is prepared; a double decomposition takes place between the salts, and, on the addition of alcohol, strontium thiosulphate, SrS_2O_3, is precipitated, which, when ignited, leaves strontium sulphide behind. The strontium sulphide thus prepared emits (when dry) a greenish-yellow light. It contains a certain amount of sulphur, sodium sulphide, and strontium sulphate. By ignition at various temperatures, and by different methods of preparation, it is possible to obtain mixtures which emit different coloured lights.

not at all the appearance of salts, and this is more especially the case with regard to the crystalline forms in which they frequently occur in nature.[29]

---

[29] As examples, we shall describe the sulphides of arsenic, antimony, and mercury. Arsenic trisulphide, or **orpiment**, As_2S_3, occurs native, and is obtained pure when a solution of arsenious anhydride in the presence of hydrochloric acid comes into contact with sulphuretted hydrogen (there is no precipitate in the absence of free acid). A beautiful yellow precipitate is then obtained: $As_2O_3 + 3H_2S = 3H_2O + As_2S_3$; it fuses when heated, and volatilises without decomposition. As_2S_3 is easily obtained in a colloidal form (Chap. I., note 57). When fused it forms a semi-transparent, yellow mass, and it is thus that it enters the market. The specific gravity of native orpiment is 3·4, and that of the artificially fused mass 2·7. It is used as a yellow pigment, and owing to its insolubility in water and acids it is less injurious than the other compounds corresponding to arsenious acid. To the type AsX_2 belongs realgar, AsS; the molecule is probably As_4S_4. **Realgar** (*sandaraca*) occurs native in brilliant red crystals of specific gravity 3·59, and may be prepared artificially by fusing together arsenic and sulphur in the proportions indicated by its formula. It is prepared in large quantities by distilling a mixture of sulphur and arsenical pyrites. Like orpiment it dissolves in calcium sulphide, and even in caustic potash. It is used for signal lights and fireworks, because it deflagrates and gives a large and very brilliant white flame with nitre.

With antimony, sulphur gives a tri- and a penta-sulphide. The former, Sb_2S_3, which corresponds with antimonious oxide, occurs native (Chap. XIX.) in a crystalline form; its sp. gr. is then 4·9, and it forms brilliant rhombic crystals of a grey colour, which fuse when heated. A substance of the same composition is obtained as an amorphous orange powder by passing sulphuretted hydrogen into an acid solution of antimonious oxide. In this respect antimonious oxide again reacts like arsenious acid, and the sulphides of both are soluble in ammonium and potassium sulphides, and, especially in the case of arsenious sulphide, are easily obtained in colloidal solutions. By prolonged boiling with water, antimonious sulphide may be entirely converted into the oxide, hydrogen sulphide being evolved (Elbers). Native antimony sulphide, or the orange precipitated trisulphide when fused with dry, or boiled with dissolved, alkalies, forms a dark-coloured mass (Kermes mineral) formerly much used in medicine, which contains a mixture of antimonious sulphide and oxide. There are also compounds of these substances. A so-called antimony vermilion is much used as a dye; it is prepared by boiling sodium thiosulphate (six parts) with antimony trichloride (five parts) and water (fifty parts). This substance probably contains an oxysulphide of antimony—that is, a portion of the oxygen in the oxide of antimony in it is replaced by sulphur. Red antimony ore, and antimony glass, which is obtained by fusing the trisulphide with antimonious oxide, have a similar composition, Sb_2OS_2. In the arts, the **antimony pentasulphide**, Sb_2S_5, is the most frequently used of the sulphur compounds of antimony. It is formed by the action of acids on the so-called Schlippe's salt, which is a **sodium thio-ortho-antimonate**, $SbS(NaS)_3$, corresponding with (Chap. XIX., note 41a) ortho-antimonic acid, $SbO(OH)_3$, with the replacement of oxygen by sulphur. It is obtained by boiling finely powdered native antimony trisulphide with twice its weight of sodium carbonate, and half its weight of sulphur and of lime, in the presence of a considerable quantity of water. The processes taking place are as follows:—The sodium carbonate is converted into hydroxide by the lime, and then forms sodium sulphide with the sulphur; the sodium sulphide then dissolves the antimony sulphide, which in this form already combines with the greatest amount of sulphur, so that a compound is formed corresponding with antimony pentasulphide dissolved in sodium sulphide. The solution is filtered and crystallised, care being taken to prevent access of air, which oxidises the sodium sulphide. This salt crystallises in large, yellowish crystals, which are easily soluble in water and have the composition $Na_3SbS_4,9H_2O$. When heated they lose their water of crystallisation and then fuse without alteration, but when in solution, and even in the crystalline form, Turning to the oxygen compounds of sulphur, mention must first be made of the fact that the acids derived from chlorine, phosphorus, and carbon are the oxidised hydrogen compounds of these elements, and therefore we can form an idea of the acid hydrates of sulphur, or of the **normal acids of sulphur,** by representing them as the oxidised products of sulphuretted hydrogen—

HCl	H_2S	H_3P	H_4C
$HClO$	H_2SO(?)	H_3PO(?)	H_4CO
$HClO_2$	H_2SO_2(?)	H_3PO_2	H_4CO_2
$HClO_3$	H_2SO_3	H_3PO_3	H_4CO_3
$HClO_4$	H_2SO_4	H_3PO_4	H_4CO_4 [30]

---

this salt turns brown in air, owing to the oxidation of the sulphur and the breaking up of the compound. As it is used in medicine, especially in the preparation of antimony pentasulphide, it is kept under a layer of alcohol, in which it is insoluble. Acids precipitate antimony pentasulphide from a solution of this salt, as an orange powder, insoluble in acids and very frequently used in medicine (*sulfur auratum antimonii*). This substance when heated evolves vapours of sulphur, and leaves antimony trisulphide behind.

Mercury forms with sulphur, compounds of the same types as those formed with oxygen. Mercurous sulphide, Hg_2S, readily splits up into mercury and mercuric sulphide. It is obtained by the action of sulphuretted hydrogen on solutions of salts of the type HgX. Mercuric sulphide, HgS, corresponding with the oxide, is **cinnabar**; it is obtained as a black precipitate by the action of an excess of sulphuretted hydrogen on solutions of mercuric salts. It is insoluble in acids, and is therefore precipitated in their presence. If a certain amount of water containing sulphuretted hydrogen is added to a solution of mercuric chloride, it first gives a white precipitate of the composition $Hg_3S_2Cl_2$—that is, a compound $HgCl,2HgS$, a sulphochloride of mercury similar to the oxychloride. But in the presence of an excess of sulphuretted hydrogen, the black precipitate of mercuric sulphide is formed. In this state it is not crystalline (the red variety is formed by the prolonged action of polysulphides of ammonium upon the black HgS), but if it is heated to its temperature of volatilisation it forms a red crystalline sublimate which is identical with native cinnabar. In this form its specific gravity is 8·0, and it forms a red powder, owing to which it is used as a red pigment (vermilion) in oil, pastel, and other paints. It is so little attacked by reagents that even nitric acid has no action on it, and the gastric juices do not dissolve it, so that it is not poisonous. When heated in air, the sulphur burns away and leaves metallic mercury. On a large scale, cinnabar is usually prepared in the following manner: 300 parts of mercury and 115 parts of sulphur are mixed together as intimately as possible and poured into a solution of 75 parts of caustic potash in 425 parts of water, and the mixture is heated at 50° for several hours. Red mercury sulphide is thus formed, and separates out from the solution. The reaction which takes place is as follows: A soluble compound, K_2HgS_2, is first formed; this compound is able to separate in colourless silky needles, which are soluble in the caustic potash, but are decomposed by water, and at 50°; this solution (perhaps by attracting oxygen from the air) slowly deposits HgS in a crystalline form.

It is worthy of remark that Linder and Picton obtained complex compounds of many of the sulphides of the heavy metals (Ca, Hg, Sb, Zn, Cd, Ag, Au) with H_2S; for example, $H_2S,7CuS$ (by the action of H_2S upon the hydrate of oxide of copper), $H_2S,9CuS$ (in the presence of acetic acid and with an excess of H_2S), &c.

[30] There are four typical hydrogen compounds, RH, RH_2, RH_3, and RH_4, and each of them has its typical oxide. Beyond H_4 and O_4 combination does not proceed (Chap. XV.).

In the case of chlorine, if not all the hydrates, at all events, salts of all the normal hydrates are known, whilst in the case of sulphur only the acids H_2S, H_2SO_3, and H_2SO_4 are known. But, on the other hand, the latter are obtained not only as hydrates, but also as stable anhydrides, SO_2 and SO_3, which are formed with the evolution of heat from sulphur and oxygen; 32 parts of sulphur in combining with 32 parts of oxygen—that is, in forming SO_2—evolve 71,000 heat units,[31] and if the oxidation proceeds to the formation of SO_3, 103,000 heat units are evolved. These figures may be compared with those which correspond with the passage of carbon into CO and CO_2, when 29,000 and 97,000 units of heat are evolved. This determines the stability of the higher oxides of sulphur, and also expresses the peculiarity of sulphur as an element which, although an analogue of oxygen, forms stable compounds with it, and thus fundamentally differs from chlorine. The higher and lower oxides of chlorine are powerful oxidising agents, whilst the higher oxide of sulphur, SO_3, has but feeble oxidising powers, and the lower oxide, SO_2, frequently acts as a reducing agent, and is formed by the direct combustion of sulphur, just as carbonic anhydride, CO_2, proceeds from the combustion of carbon. In the combustion of sulphur, and also in the oxidation (roasting) of the sulphides and polysulphides by their ignition in air, sulphurous oxide, or **sulphurous anhydride** or **sulphur dioxide**, SO_2,[31a] is exclusively formed. It is prepared on a large scale, by burning sulphur or roasting iron pyrites or other sulphides,[32] for the manufacture of sulphuric acid (Chap. VI.), and for direct application in the manufacture of wine, for bleaching tissues and for other purposes. In the latter instances its application is based on the fact that sulphurous anhydride acts on certain vegetable matters, and has the property of a reducing and feeble acid.[32a]

---

[31] Rhombic sulphur, 71,080 heat units; monoclinic sulphur, 71,720 units, according to Thomsen.

[31a] However, when sulphur or metallic sulphides burn in an excess of air, there is always formed a certain, although small, amount of SO_3, which gives sulphuric acid with the moisture of the air.

[32] The enormous amount of sulphuric acid now manufactured is chiefly prepared by roasting native pyrites, but a considerable amount of the SO_2 used for this purpose is obtained by roasting zinc blende (ZnS) and copper and lead sulphides. A certain amount is also procured from soda refuse (note 6) and from the residues obtained from the purification of coal gas.

[32a] Sulphurous anhydride is also obtained by the decomposition of many sulphates, especially of the heavy metals, by the action of heat; but this requires a very powerful heat. This formation of sulphurous anhydride from sulphates is based on the decomposition proper to sulphuric acid itself. When sulphuric acid is strongly heated (for instance, by dropping it upon an incandescent surface) it is decomposed into water, oxygen, and sulphurous anhydride—that is, into those compounds from which it is

In the laboratory—that is, on a small scale—sulphurous anhydride is best prepared by deoxidising sulphuric acid by heating it with charcoal, or with copper, sulphur, mercury, &c. Charcoal produces this decomposition of sulphuric acid at but moderately high temperatures; it is itself converted into carbonic anhydride,[32b] so that when sulphuric acid is heated with charcoal it evolves a mixture of sulphurous and carbonic anhydrides: $C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O$. The metals which are unable to decompose water, and which do not, therefore, expel hydrogen from sulphuric acid, are frequently capable of decomposing sulphuric acid, with the evolution of sulphurous anhydride, just as they decompose nitric acid, forming the lower oxides of nitrogen. These metals are silver, mercury, copper, lead, and others. Thus, for example, the action of copper on sulphuric acid may be expressed by the following equation: $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$. In the laboratory this reaction is carried on in a flask with a gas-conducting tube, and does not take place unless aided by heat.[33]

In its physical and chemical properties sulphurous anhydride presents a great **resemblance to carbonic anhydride.** It is a heavy gas, somewhat considerably soluble in water, very easily condensed into a liquid; it forms normal and acid salts, does not evolve oxygen under the direct action of heat,[34] although such metals as sodium and magnesium burn in it, just as in carbonic anhydride. It has a suffocating odour, which is well known owing to its being evolved when sulphur or sulphur matches are burnt. In characterising the properties of sulphurous anhydride, it is very important to remember (Chap. II.) also that it is more easily liquefied (at −10°, or at 0° under two atmospheres pressure) than carbonic anhydride (thirty-six atmospheres

---

formed. A similar decomposition proceeds during the ignition of many sulphates. Even so stable a sulphate as gypsum does not resist the action of very high temperatures, but is decomposed in the same manner, lime being left behind. The decomposition of sulphates by heat is accomplished with still greater facility in the presence of sulphur, because in this case the liberated oxygen combines with the sulphur and the metal is able to form a sulphide. Thus when ferrous sulphate (green vitriol) is ignited with sulphur, it gives ferrous sulphide and sulphurous anhydride: $FeSO_4 + 2S = FeS + 2SO_2$. At 400° sulphuric acid and sulphur give an extremely uniform stream of pure sulphurous anhydride, so that it is best prepared on a manufacturing scale by this method. Iron pyrites, FeS_2, when heated to 150° with sulphuric acid (sp. gr. 1·75) in cast-iron vessels, also gives an abundant and uniform supply of sulphurous anhydride.

[32b] Mellitic acid is formed at the same time (Verneuille).

[33] The thermochemical data connected with this reaction are as follows: A molecule of hydrogen, H_2, in combining with oxygen ($O = 16$), develops about 69,000 heat units—whilst the molecule of SO_2 in combining with oxygen only develops about 32,000 heat units—that is, about half as much—and therefore those metals which cannot decompose water may still be able to deoxidise sulphuric into sulphurous acid.

[34] That is, it only dissociates and re-forms the original product on cooling.

at 0°),[35] that it is more soluble than carbonic anhydride (Vol. I., p. 79): at 0°, 100 vols. of water dissolve 180 vols. of carbonic anhydride and 688 vols. of sulphuric anhydride; that the molecular weight of SO_2 is 64, and that of CO_2, 44, and that the density of liquid sulphurous anhydride at 0° is 1·43 (molecular volume=45) and that of carbonic anhydride, 0·95 (molecular volume=49). Although sulphur dioxide is the anhydride of an acid, nevertheless, like carbonic anhydride, it does not form any stable compounds with water, but gives a solution from which it may be entirely expelled by the action of heat.[36] The acid character of sulphurous anhydride is clearly expressed by the fact that it is entirely absorbed by alkalies, with which it forms acid and normal salts readily soluble in water. With salts of barium, calcium, and the heavy metals, the normal salts of the alkalies, M_2SO_3, give precipitates exactly like those formed by the carbonates. In general, the salts of sulphurous acid are closely analogous to the corresponding carbonates.

One of the most widely used salts, **acid sodium sulphite**, $NaHSO_3$, may be obtained by passing sulphurous anhydride into a solution of sodium hydroxide. It is also formed by saturating a solution of sodium carbonate with the gas (carbonic anhydride is then given off), and as the solubility of the acid sulphite is much greater than that of the carbonate, a further quantity of the latter may be dissolved after the passage of the sulphurous anhydride, so that in this manner a very strong solution of the sulphite may be ultimately formed, from which it may be obtained in a crystalline form, either by cooling and evaporating (without heating, for then the salt would give off sulphurous anhydride) or by adding alcohol to the solution. When exposed to the air this salt loses sulphurous anhydride and attracts oxygen, which converts it into sodium sulphate. The acid sulphites of the alkali metals are able to combine not only with oxygen, but also with many other substances—for example, a solution of the sodium salt dissolves sulphur, forming sodium thiosulphate, gives crystalline compounds with the aldehydes and ketones, and dissolves many bases, converting them into double sulphites. Having the power of attracting or

---

[35] At a given temperature the pressure of this gas evolved from any salt will be less than that of carbonic anhydride, if we compare the separation of a gas from its salts with the phenomenon of evaporation, as was done in discussing the decomposition of calcium carbonate.

Liquid sulphurous anhydride is used on a large scale (Pictet) for the production of cold.

[36] De la Rive, Pierre, and more especially Roozeboom, have investigated the crystallo-hydrate which is formed by sulphurous anhydride and water at temperatures below 7° under the ordinary pressure, and in closed vessels (at temperatures below 12°). Its composition is $SO_2,7H_2O$, and its density 1·2. This hydrate corresponds with the similar hydrate $CO_2,8H_2O$ obtained by Wroblewsky.

absorbing oxygen, acid sodium sulphite is also able to absorb chlorine, and is therefore employed, like sodium thiosulphate, for the removal of chlorine (as an antichlor), especially in the bleaching of fabrics, when it is necessary to remove the last traces of the chlorine held in the tissues, which might otherwise have an injurious effect on them. If a solution of an alkali hydroxide is divided into two parts, and one half is saturated with sulphurous anhydride, and the other half then added to it, a normal salt will be obtained in the solution, having an alkaline reaction, like a solution of sodium carbonate. The acid salt has a neutral reaction.[36a] Like sodium carbonate, **normal sodium sulphite** has the composition $Na_2SO_3,10H_2O$, and its maximum solubility is at 33°—in a word, it very closely resembles sodium carbonate. Although this salt does not give off sulphurous anhydride from its solution, it is able, like the acid salt, to absorb oxygen from the air, and is then converted into sodium sulphate.[37]

Besides the acid character we must also point out the reducing character of sulphurous anhydride. The **reducing action** of sulphurous acid, its anhydride and salts, is due to their property of passing into sulphuric acid and sulphates. The reducing action of the sulphites is particularly energetic, so that they even convert nitric oxide into nitrous oxide: $K_2SO_3+2NO=K_2SO_4+N_2O$. The salts of many of the higher oxides are converted into those of the lower—for example, FeX_3 into FeX_2, CuX_2 into CuX, HgX_2 into HgX; thus, $2FeX_3+SO_2+2H_2O=2FeX_2+H_2SO_4+2HX$. In the presence of water, sulphurous anhydride is oxidised by chlorine ($SO_2+2H_2O+Cl_2=H_2SO_4+2HCl$),

---

[36a] Schwicker (1889), by saturating $NaHSO_3$ with potash, or $KHSO_3$ with soda, obtained $NaKSO_3$ (in general sulphurous acid easily forms double salts), in the first instance with H_2O, and in the second instance with $2H_2O$. This is probably owing to the different media in which the crystals are formed, but is not infrequently regarded as due to the different characters of the two hydrogens of sulphurous acid, which is admissible if sulphurous and sulphuric acids are composed of one and the same residue, 'sulphoxyl,' (see further on) HSO_3, combined with H or HO. And if sulphurous acid is $H(SO_3H)$, that is, $HSO_2(OH)$, the two hydrogens in its molecule would be of different character, one being directly combined with S, and the other through the medium of oxygen in the form OH. In this case one of the above salts will be KSO_3ONa and the other $NaSO_3OK$; that is to say, they are isomeric. It cannot be denied that this view is highly probable, especially as it simplifies the explanation of certain reactions of sulphurous acids, but still, in my opinion, there can be no certainty of this being the case, for there exists a chloranhydride, $SOCl_2$, which is equivalent to sulphurous acid, $SO(OH)_2$, with the substitution of OH by chlorine, and yet nothing indicates the possibility of two isomeric chloranhydrides, $ClSO_2OH$ and HSO_2OCl. For my part, I consider that the isomerism of the above two salts cannot be considered as proved, and that it is therefore impossible to be quite certain of it.

[37] The normal salts of calcium and magnesium are slightly, and the acid salts freely, soluble in water. These acid sulphites are much used in practice; thus, calcium bisulphite is employed in the manufacture from sawdust of cellulose, which is largely made use of for mixing with fibrous matter in the manufacture of paper.

iodine, nitrous acid, hydrogen peroxide, hypochlorous acid, chloric acid, and other oxygen compounds of the halogens, chromic, manganic, and many other metallic acids and higher oxides, as well as all peroxides. Free oxygen in the presence of spongy platinum is able to oxidise sulphurous anhydride even in the absence of water, in which case sulphuric anhydride, SO_3, is formed, so that the latter may be prepared by passing a mixture of sulphurous anhydride and oxygen over incandescent spongy platinum, or, as it is prepared on a large scale in chemical works (Winkler's process), by passing this mixture over asbestos or pumice-stone moistened with a solution of a platinum salt and ignited. Sulphurous anhydride is completely absorbed by certain higher oxides—for instance, by barium peroxide and lead dioxide ($PbO_2 + SO_2 = PbSO_4$).[38]

There are, however, cases where sulphurous anhydride acts as an oxidising agent—that is, it is **deoxidised** in the presence of substances which are capable of absorbing oxygen with still greater energy than the sulphurous anhydride itself. This oxidising action proceeds with the formation of sulphuretted hydrogen or of sulphides, while the reducing agent is oxidised at the expense of the oxygen of the sulphurous anhydride. Thus stannous chloride, $SnCl_2$, in an aqueous solution gives a precipitate of stannic sulphide, SnS_2, with sulphurous anhydride—that is, the latter is deoxidised to sulphuretted hydrogen, while SnX_2 is oxidised into SnX_4. A solution of sulphurous anhydride, in acting on zinc, which passes into solution, does not evolve hydrogen, but combines directly,[39] forming a salt of **hydrosulphurous**

---

[38] This reaction is taken advantage of for removing sulphurous anhydride from a mixture of gases. Lead dioxide, PbO_2, is brown, and when combined with sulphurous anhydride it forms lead sulphate, $PbSO_4$, which is white, so that the reaction is evident from both the change in colour and the development of heat. Sulphurous anhydride is slowly decomposed by the action of light, with the separation of sulphur and formation of sulphuric anhydride. This explains the fact that sulphurous anhydride prepared in the dark gives a white precipitate of silver sulphite, Ag_2SO_3, with silver perchlorate, $AgClO_4$, but when prepared in the light, even in diffused light, it gives a dark precipitate. This naturally depends on the fact that the sulphur liberated then forms silver sulphide, which is black. It is notable that SO_2 combines directly with some salts, for instance, KI (Peshar, 1900), KCNS (Fox, 1902), &c.

[39] Schönbein observed that the liquid turns yellow, and acquires the faculty of **decolorising** litmus and indigo. Schützenberger showed that this depends on the formation of a zinc salt of a peculiar and very powerfully reducing acid, for with cupric salts the yellow solution gives a red precipitate of cuprous hydride or metallic copper, and it completely reduces salts of silver and mercury. An exactly similar solution is obtained by the action of zinc on sodium bisulphite without access of air and in the cold. The yellow liquid absorbs oxygen from the air with great avidity, and forms a sulphate. If a solution of $NaHSO_3$ be treated with zinc dust in the presence of an excess of SO_2 $2(NaHSO_3 + Zn + SO_2 = ZnSO_3 + Na_2S_2O_4 + H_2O)$ and be then precipitated with lime, the filtrate will contain the sodium salt. With NaCl strong solutions deposit crystals, which should be kept and dried without access of air. The solution of these crystals has the

acid, ZnS_2O_4. The free acid is still less stable than the salt ($H_2S_2O_4 = H_2 + 2SO_2$).

The faculty of sulphurous anhydride of combining with various substances is evident from its compounds with hydrogen and with oxygen, and also appears in the fact that, like carbonic oxide, it combines with chlorine, forming a chloranhydride of sulphuric acid, SO_2Cl_2, to which we shall afterwards return. The same faculty for combination also appears in the exceedingly characteristic formation of a peculiar series of salts obtained by Pelouze and Frémy. At a temperature of −10° or below, nitric oxide, NO, is absorbed by alkaline solutions of the alkali sulphites, forming a peculiar series of **nitrosulphates.** At a higher temperature these salts are not formed, but the nitric oxide is reduced to nitrous oxide. But in the cold, and after a certain time, the liquid saturated with nitric oxide gives prismatic crystals resembling those of nitre. The composition of the potassium salt is $K_2SN_2O_5$—that is, the salt contains the elements of potassium sulphite and of nitric oxide.[40]

above-mentioned decolorising and reducing properties. These crystals contain a sodium salt of a lower acid which is called *hydrosulphurous acid* ($= H_2 + 2SO_2$); their composition was at first supposed to be $HNaSO_2$, but it was afterwards proved that they do not contain hydrogen, and present the composition $Na_2S_2O_4 + 2H_2O$ (Bernthsen). The same salt is formed by the action of a galvanic current on a solution of sodium bisulphite, owing to the action of the hydrogen at the moment of its liberation. If SO_2 resembles CO_2 in its composition, then hyposulphurous acid, $H_2S_2O_4$, resembles oxalic acid, $H_2C_2O_4$. Perhaps an analogue of formic acid, SH_2O_2, will be discovered. Moissan (1902) showed that potassium hydride and also the hydrides of Na, Li, Sr, &c., directly absorb SO_2 if it is in a state of dilution or rarefaction (otherwise an explosion will ensue), forming salts of hydrosulphurous acid with the evolution of hydrogen, $2KH + 2SO_2 = K_2S_2O_4 + H_2$.

[40] The instability of this salt is very great, and may be compared with that of the compound of ferrous sulphate with nitric oxide, for when heated under the contact influence of spongy platinum, charcoal, &c., it splits up into potassium sulphate and nitrous oxide. At 180° the dry salt gives off nitric oxide, and re-forms potassium sulphite. The free acid has not yet been obtained. These salts resemble the **sulphonitrites** discovered by Frémy in 1845. They are obtained by passing sulphurous anhydride through a concentrated and strongly alkaline aqueous solution of potassium nitrite. They are soluble in water, but are precipitated by excess of alkali. The first product of the action has the composition $K_3NS_3O_9$. It is then converted by the further action of sulphurous anhydride, water, and other reagents into a series of similar complex salts, many of which give well-formed crystals. One must suppose that the chief cause of the formation of these very complex compounds is that they contain unsaturated compounds, NO, KNO_2, and $KHSO_3$, all of which are subject to oxidation and further combination, and therefore easily combine among each other. The decomposition of these compounds, when their solutions are heated, is due to the fact that the deoxidant, sulphurous anhydride, reduces the nitrous acid, NO(OH), to ammonia. In my opinion the composition of the sulphonitrites may be very simply referred to the composition of ammonia, in which the hydrogen is replaced by the radicle of the sulphates. If we represent the composition of potassium sulphate as $KO{\cdot}KSO_3$, the group KSO_3 will be equivalent (according to the law of substitution) to HO and to hydrogen. With hydrogen, it forms acid potassium sulphite, $KHSO_3$. Hence the group KSO_3 may also replace the hydrogen in ammonia. Judging by my analysis (1870), the extreme limit of this substitution,

There are also several other substances, formed by the oxides of nitrogen and sulphur, which belong to this class of complex and, under some circumstances, unstable compounds. In the manufacture of sulphuric acid, both these classes of oxides come into contact with each other in the lead chambers, and if there be insufficient water for the formation of sulphuric acid they give crystalline compounds, termed **chamber crystals**. As a rule, the composition of the crystals is expressed by the formula $NHSO_5$. This is a compound of the radicles NO_2, of nitric acid, and HSO_3, of sulphuric acid, or **nitrosulphuric acid**, $NO_2{\cdot}SHO_3$, if sulphuric acid be expressed as $OH{\cdot}SHO_3$ and nitric acid by $NO_2{\cdot}OH$. This substance is best understood as sulphurous acid, SH_2O_3, in which one hydrogen is replaced by the residue of nitric acid, $NO_2 : S(NO_2)HO_3$. The tabular crystals of this substance fuse at about 70°, and are formed by the direct action of both nitrous anhydride and nitric peroxide (but not NO, which is not absorbed by sulphuric acid) on sulphuric acid (Weltzien and others), and especially on sulphuric acid containing an anhydride and the lower oxides of sulphur and nitric acid.[41]

$N(HSO_3)_3$, agrees with that of the sulphonitrite, which is easily formed, simultaneously with alkali, by the action of potassium sulphite on potassium nitrite, according to the equation: $3K(KSO_3) + KNO_2 + 2H_2O = N(KSO_3)_3 + 4HKO$. The researches of Berglund, and especially of Raschig (1887), fully verified my conclusions, and showed that we must distinguish the following types of salts, corresponding with ammonia, where X stands for the sulphonic group, HSO_3, in which the hydrogen is replaced by potassium and is hence KSO_3: (1) NH_2X, (2) NHX_2, (3) NH_3, (4) $N(OH)XH$, (5)$N(OH)X_2$, (6) $N(OH)_2X$, just as $NH_2(OH)$ is hydroxylamine, $NH(OH)_2$, the hydrate of nitrous oxide, and $N(OH)_3$, orthonitrous acid, as follows from the law of substitution. This class of compounds is in most intimate relation with the amides of sulphuric acid and with the series of sulphonitrous compounds, corresponding with 'chamber crystals' and their acids, which we shall consider later. The researches of Divers and his assistants explained the relations of the substances formed to the ammonia derivatives. As an instance, we may mention that when a solution of $2HNaSO_3$ with $NaNO_2$ is cooled to 0° it gives NaHO and a salt, $N(OH)(NaSO_3)_2$, which is very soluble, and gives a less soluble salt with KCl. On boiling, a solution of this salt first gives $KHSO_4 + NH(OH)(KSO_3)$ and then the whole of the potassium is converted into sulphate: $N(OH)(KSO_3)_2 + 2H_2O = K_2SO_4 + NH_2(OH)H_2SO_4$ (sulphate of hydroxylamine). With sulphurous oxide, a strong solution of hydrochloride of hydroxylamine forms directly a crystalline, slightly soluble mono-substituted acid, $NH_2SO_3H = NH_2OH + SO_2$. With water the di- and tri-substituted acids NHX_2 and NX_3 readily form H_2SO_4 and the mono-substituted acid. The di-substituted acid, NHX_2, is easily formed by the action of NH_3 on the first chloranhydride of sulphuric acid, SO_3HCl. Compounds containing hydroxyl, for instance, $N(OH)X_2$ are, as a rule, formed by the action of nitric acid, which, in the aspect of an ortho-hydrate, is equivalent to $N(OH)_3$.

[41] Nitroso-sulphuric acid, $NHSO_5$, readily crystallises, melts at 73°, gives a chloranhydride and anhydride (see later); but it does not form any salts, because it is decomposed by water and still more easily by alkalies. In the sulphuric acid chambers the lower oxides of nitrogen and sulphur take part in the reaction. They are oxidised by the oxygen of the air, and form nitro-sulphuric acid—for example, $2SO_2 + N_2O_3 + O_2 + H_2O = 2NHSO_5$. This compound dissolves in strong sulphuric acid without changing, and

Thiosulphuric acid, $H_2S_2O_3$—that is, a compound of sulphurous acid and sulphur—also belongs to the products of combination of sulphurous acid. In the same way that sulphurous acid, H_2SO_3, gives H_2SO_4 with oxygen, so it gives $H_2S_2O_3$ with sulphur. In a free state it is very unstable, and it is only known in the form of its salts, which proceed from the direct action of sulphur on the normal sulphites; if endeavours are made to separate it in a free state, it immediately splits up into those elements from which it might be formed—that is, into sulphur and sulphurous acid. The most important of its salts is **sodium thiosulphate** (known as hyposulphite), $Na_2S_2O_3,5H_2O$, which occurs in colourless crystals, and is unacted on by atmospheric oxygen either when in a dry state or in solution. Many other salts of this acid are easily formed by means of this one,[41a] although this cannot be done with all bases, for such of the latter as alumina, ferric oxide, chromium oxide, and others do not give compounds with thiosulphuric acid, just as they do not form stable compounds with carbonic acid. Whenever these salts might be formed, they (like the acid) split up into sulphurous acid and sulphur, and furthermore the elements of thiosulphuric acid in many cases act in a reducing manner, forming sulphuric acid and taking up the oxygen from reducible oxides. Thus, when treated with a thiosulphate the soluble ferric salts give a precipitate of sulphur and form ferrous salts. The thiosulphates of the metals of the alkalies are obtained directly by boiling a solution of their sulphites with sulphur: $Na_2SO_3 + S = Na_2S_2O_3$. The same salts are formed by the action of sulphurous anhydride on solutions of the sulphides; thus, sodium sulphide dissolved in water gives sulphur and sodium thiosulphate

---

when such a solution is diluted (when the sp. gr. falls to 1·5), it splits up into sulphuric acid and nitrous anhydride, and by the action of sulphurous anhydride is converted into nitric oxide, which by itself (in the absence of nitric acid or oxygen) is insoluble in sulphuric acid. These reactions are taken advantage of in retaining the oxides of nitrogen in the Gay-Lussac coke-towers, and for extracting the absorbed oxides of nitrogen from the resultant solution in the Glover tower. Although nitric oxide is not absorbed by sulphuric acid, it reacts (Rose, Brüning) on its anhydride, and forms sulphurous anhydride and a crystalline substance, $N_2S_2O_9 = 2NO + 3SO_3 - SO_2 = N_2O_3,2SO_3$. This may be regarded as the anhydride of nitro-sulphuric acid, because $N_2S_2O_9 = 2NHSO_5 - H_2O$; it melts at 217°, and, like nitro-sulphuric acid, is decomposed by water into nitro-sulphuric acid and nitrous anhydride. Since boric and arsenious anhydrides, alumina, and other oxides of the form R_2O_3 are able to combine with sulphuric anhydride to form similar compounds decomposable by water, the above compound does not present any exceptional phenomenon. Sulphuric anhydride also combines with NO_2, forming $N_2O_4,2SO_3$, which under the action of heat evolves oxygen and gives the above anhydride, $N_2S_2O_9$. The substance, $NOCl,SO_3$, obtained by Weber by the action of nitrosyl chloride upon sulphuric anhydride belongs to this class of compounds. But with H_2SO_4 the nitrosyl chloride gives also $NHSO_5$ with the evolution of HCl.

[41a] Many double salts of thiosulphuric acid are known; for instance, $PbS_2O_3,8Na_2S_2O_3,12H_2O$; $CaS_2O_3,3K_2S_2O_3,5H_2O$, &c. (Fortman, Schwicker, Fock, and others).

when a stream of sulphurous anhydride is passed through it: $2Na_2S + 3SO_2 = 2Na_2S_2O_3 + S$. The polysulphides of the alkali metals, when left exposed to the air, attract oxygen and also form thiosulphates.[42] A mixture of solutions of Na_2S and Na_2SO_4 gives $2NaI$ and $Na_2S_2O_3$ under the action of iodine.

---

[42] Thus, when alkali waste, which contains calcium sulphide, undergoes oxidation in the air, it forms first a calcium polysulphide, and then calcium thiosulphate, CaS_2O_3. When iron or zinc acts on a solution of sulphurous acid, besides the hyposulphurous acid first formed, a mixture of sulphite and thiosulphate is obtained (note 39), $3SO_2 + Zn_2 = ZnSO_3 + ZnS_2O_3$. In this case, as in the formation of hyposulphurous acid, there is no hydrogen liberated. One of the most common methods for preparing thiosulphates consists in the **action of sulphur on the alkalies**. The reaction is accomplished by the formation of sulphides and thiosulphates, just as the reaction of chlorine on alkalies is accompanied by the formation of hypochlorites and chlorides; hence, in this respect, the thiosulphates hold the same position in the order of the compounds of sulphur as the hypochlorites do among the chlorine compounds. The reaction of caustic soda on an excess of sulphur may be expressed thus: $6NaHO + 12S = 2Na_2S_5 + Na_2S_2O_3 + 3H_2O$. Thus sulphur is soluble in alkalies. On a large scale sodium thiosulphate, $Na_2S_2O_3$, is prepared by first heating sodium sulphate with charcoal, to form sodium sulphide, which is then dissolved in water and treated with sulphurous anhydride. The reaction is complete when the solution has become slightly acid. A certain amount of caustic alkali is added to the slightly acid solution; a portion of the sulphur is thus precipitated, and the solution is then boiled and evaporated, when the salt crystallises out. Sodium thiosulphate is also prepared by the double decomposition of the soluble calcium thiosulphate with sodium sulphate or carbonate, in which case calcium sulphate or carbonate is precipitated. The calcium thiosulphate is prepared by the action of sulphurous anhydride on either calcium sulphide or alkali waste.

The crystals of sodium thiosulphate, $Na_2S_2O_3,5H_2O$, are stable, do not effloresce, and at 0° dissolve in one part of water, and at 20° in 0·6 part. The solution of this salt does not undergo any change when boiled for a short time, but after prolonged boiling it deposits sulphur. The crystals fuse at 56°, and lose all their water at 100°. When the dry salt is ignited it gives sodium sulphide and sulphate. With acids, a solution of the thiosulphate soon becomes cloudy and deposits an exceedingly fine powder of sulphur (note 10). If the amount of acid added is considerable, it also evolves sulphurous anhydride: $H_2S_2O_3 = H_2O + S + SO_2$. Sodium thiosulphate has many practical uses; it is used in photography for dissolving silver chloride and bromide. Its solvent action on silver chloride may be taken advantage of in extracting this metal as chloride from its ores. In dissolving, it forms a double salt of silver and sodium: $AgCl + Na_2S_2O_3 = NaCl + AgNaS_2O_3$. Sodium thiosulphate is an **antichlor**—that is, a substance which hinders the destructive action of free chlorine—owing to its being very easily oxidised by chlorine into sulphuric acid and sodium chloride. The reaction with iodine is different, and is remarkable for the accuracy with which it proceeds. The iodine takes up half the sodium from the salt and converts it into a tetrathionate, $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$, and hence this reaction is employed for the determination of free iodine. As iodine is expelled from potassium iodide by chlorine, it is possible also to determine the amount of chlorine by this method if potassium iodide be added to a solution containing chlorine. And as many of the higher oxides are able to evolve iodine from potassium iodide, or chlorine from hydrochloric acid (for example, the higher oxides of manganese, chromium, &c.), it is also possible to determine the amounts of these higher oxides by means of sodium thiosulphate and liberated iodine. This forms the basis of the **iodometric methods** of volumetric analysis. The details of these methods will be found in works on analytical chemistry.

On adding a solution of a **lead salt** gradually to a solution of sodium thiosulphate, a white precipitate of lead thiosulphate, PbS_2O_3, is formed (a soluble double salt is first

Although sulphur, oxidising at a high temperature, only forms a small quantity of sulphuric anhydride, SO_3, and nearly all passes into sulphurous anhydride, still the latter may be converted into the higher oxide, or **sulphuric anhydride**, SO_3, by many methods. Sulphuric anhydride is a solid crystalline substance at the ordinary temperature; it is easily fusible (15°) and volatile (46°), and rapidly attracts moisture. Although it is formed by the combination of sulphurous anhydride with oxygen, it is very prone to further combination, for instance, with water, hydrochloric acid, ammonia, many hydrocarbons, and even with sulphuric acid, boric and nitrous anhydrides, &c., and also with bases which burn directly in its vapour, forming sulphates in the presence of traces of moisture (see Chap. IX., note 29).[42a] The oxidation of sulphurous anhydride, SO_2, into sulphuric anhydride, SO_3, is effected by passing a mixture of the former and dry oxygen or air over incandescent spongy platinum. An increase of pressure accelerates the reaction (Hänisch). If the product is passed into a cold vessel, crystalline sulphuric anhydride is deposited upon the sides of the vessel; but as it is difficult to avoid all traces of moisture it always contains compounds of its hydrates, $H_2S_2O_7$ and $H_2S_4O_{13}$, whose presence so modifies the properties of the anhydride (Weber) that formerly two modifications of the anhydride were recognised. The same sulphuric anhydride may be obtained from certain anhydrous or almost anhydrous, sulphates, which are decomposed by heat, whilst an impure but perfectly anhydrous anhydride is formed by distillation over phosphoric anhydride. For instance, acid sodium sulphate, $NaHSO_4$, and the pyro- or di-sulphate, $Na_2S_2O_7$ (Chap. XII), formed from it, evolve sulphuric anhydride when ignited. Green vitriol—that is, ferrous sulphate, $FeSO_4$—belongs to the number of those sulphates which easily give off sulphuric anhydride under the action of heat. It contains water of crystallisation and parts with it when heated, but the last equivalent of water is driven off with

---

formed, and if the action is rapid, lead sulphide). When this substance is heated at 200°, it undergoes a change and takes fire. In solution sodium thiosulphate rapidly reduces cupric salts to cuprous salts by means of the sulphurous acid contained in the thiosulphate, but the resultant cuprous oxide is not precipitated, because it passes into the state of a thiosulphate and forms a double salt. These double cuprous salts are excellent reducing agents. The solution, when heated, gives a black precipitate of copper sulphide.

At one time it was thought that all the salts of thiosulphuric acid only existed in combination with water, and it was then supposed that their composition was $H_4S_2O_4$, or H_2SO_2, but Popp obtained the anhydrous salts.

[42a] Liquid SO_3 dissolves flowers of sulphur and deposits a blue substance to which the composition S_2O_3 is ascribed, but which is not stable and readily decomposes into SO_2 and S (Weber, 1891). Nothing further is known about this substance. Selenium and tellurium give $SSeO_3$ and $STeO_3$ with SO_3.

difficulty, just as is the case with magnesium sulphate, $MgSO_4,7H_2O$; however, when thoroughly heated, this evolution of sulphuric anhydride does take place, although not completely, because at a high temperature a portion of it is decomposed by the ferrous oxide (SO_3+2FeO), which is converted into ferric oxide, Fe_2O_3, and in consequence part of the sulphuric anhydride is converted into sulphurous anhydride. Thus, the products of the decomposition of ferrous sulphate will be: ferric oxide, Fe_2O_3, sulphurous anhydride, SO_2, and sulphuric anhydride, SO_3, according to the equation: $2FeSO_4=Fe_2O_3+SO_2+SO_3$. As water still remains with the ferrous sulphate when it is heated, the result will partially consist of the hydrate H_2SO_4, with anhydride, SO_3, dissolved in it. Sulphuric acid was for a long time prepared in this manner; the process was formerly carried on on a large scale in the neighbourhood of Nordhausen, and hence the sulphuric acid prepared from ferrous sulphate is called **fuming** or **Nordhausen acid.** At the present time the fuming acid is prepared by passing the volatile products of the decomposition of ferrous sulphate through strong sulphuric acid prepared by the ordinary method. The sulphurous anhydride is insoluble in it, but it absorbs the sulphuric anhydride. Sulphuric anhydride may be prepared not only by igniting $FeSO_4$ or sodium pyrosulphate, $Na_2S_2O_7$ (the decomposition proceeds at 600°), but also by heating a mixture of the latter and $MgSO_4$ (Walters); in the former case a stable double salt, $MgNa_2(SO_4)_2$, finally remains. It is also obtained by the direct combination of SO_2 and O under the action of spongy platinum or asbestos coated with platinum black. Nordhausen sulphuric acid fumes in air, owing to its containing and easily giving off sulphuric anhydride, and it is therefore also called **fuming sulphuric acid**; these fumes are nothing but the vapour of sulphuric anhydride combining with the moisture in the air and forming non-volatile sulphuric acid (hydrate).[13]

---

[13] Nordhausen sulphuric acid may serve as a very simple means for the preparation of sulphuric anhydride. For this purpose the Nordhausen acid is heated in a glass retort, whose neck is firmly fixed in the mouth of a well-cooled flask. The access of moisture is prevented by connecting the receiver with a drying-tube. On heating the retort, the vapours of sulphuric anhydride will pass over into the receiver, where they condense; the crystals of anhydride thus prepared will, however, contain traces of sulphuric acid—that is, of the hydrate. By repeatedly distilling over phosphoric anhydride, it is possible to obtain the pure anhydride, SO_3, especially if the process be carried on without access of air in a closed vessel.

The ordinary sulphuric anhydride, which is imperfectly freed from the hydrate, is a snow-white, exceedingly volatile substance, which crystallises (generally by sublimation) in long silky prisms, and only gives the pure anhydride when carefully distilled over P_2O_5. Freshly prepared crystals of almost pure anhydride fuse at 16° into a colourless liquid having a specific gravity 1·91 at 26°, and 1·81 at 47°; it volatilises at 46°. After being kept for some time, the anhydride, even when containing only small traces of water, Nordhausen sulphuric acid contains a peculiar compound of SO_3 and H_2SO_4, or **pyrosulphuric acid** ; an imperfect anhydride of sulphuric acid, $H_2S_2O_7$, analogous in composition with the salts $Na_2S_2O_7$, $K_2Cr_2O_7$, and bearing the same relation to H_2SO_4 that pyrophosphoric acid does to H_3PO_4. The bond holding the sulphuric acid and anhydride together is unstable. This is obvious from the fact that the anhydride may easily be separated from this compound by the action of heat. In order to obtain the definite compound, the Nordhausen acid is cooled to 5°, or, better still, a portion of it is distilled until all the anhydride and a certain amount of sulphuric acid have passed over into the distillate, which will then solidify at the ordinary temperature, because the compound H_2SO_4,SO_3 fuses at 35°. Although this substance reacts on water, bases, &c., like a mixture of $SO_3 + H_2SO_4$, still since a definite compound, $H_2S_2O_7$, exists in a free state and gives salts and a chloranhydride, $S_2O_5Cl_2$,[44] we must admit the existence of a definite pyrosulphuric acid, like pyrophosphoric acid, only that the latter has far greater stability and is not even converted into a perfect hydrate by water. Further, the salts $M_2S_2O_7$ dissolved in water react in the same manner as the acid salts $MHSO_4$, whilst the imperfect

---

undergoes a change of the following nature: A small quantity of sulphuric acid combines by degrees with a large proportion of the anhydride, forming polysulphuric acids, H_2SO_4,nSO_3, which fuse with difficulty (even at 100°, Marignac), but decompose when heated. In the entire absence of water this rise in the fusing-point does not occur (Weber), and then the anhydride long remains liquid, and solidifies at about +15°, volatilises at 40°, and has a specific gravity 1·94 at 16°. The infusible anhydride, obtained by keeping the ordinary anhydride, has the appearance of silky crystals, which many chemists still regard as a polymeric variety, although from Weber's researches it is more likely to be a polyhydrate, $H_2SO_4(SO_3)_n$, as was stated above.

[44] Pyrosulphuric chloranhydride, or **pyrosulphuryl chloride**, $S_2O_5Cl_2$, corresponds with pyrosulphuric acid, in the same way that sulphuryl chloride, SO_2Cl_2, corresponds with sulphuric acid. With SO_3 the latter gives $S_2O_5Cl_2 = SO_2Cl_2 + SC_3$. It is also obtained by the action of the vapour of sulphuric anhydride on sulphur chloride: $S_2Cl_2 + 5SO_3 = 5SO_2 + S_2O_5Cl_2$. It (and not sulphuryl chloride, SO_2Cl_2, Michaelis) is also formed by the action of phosphorus pentachloride in excess on sulphuric acid (or its first chloranhydride, SHO_3Cl). It is an oily liquid, boiling at about 150°, and of sp. gr. 1·8. According to Konovaloff (Chap. VII.), its vapour density is normal. It should be noticed that the same substance is obtained by the action of sulphuric anhydride on sulphur tetrachloride, and also on carbon tetrachloride, and this substance is the last product of the metalepsis of CH_4, and therefore the comparison of SCl_2 and S_2Cl_2 with products of metalepsis (see later) also finds confirmation in particular reactions. Rose, who obtained pyrosulphuryl chloride, $S_2O_5Cl_2$, regarded it as $SCl_6,5SO_3$, for at that time an endeavour was always made to find two component parts of opposite polarity, and this substance was cited as a proof of the existence of a hexachloride, SCl_6. Pyrosulphuryl chloride is decomposed by cold water, but more slowly than chlorosulphuric acid and the other chloranhydrides.

The relation between pyrosulphuric acid and the normal acid will be obvious if we express the latter by the formula $OH(SO_3H)$, because the sulphonic group (SO_3H) is then evidently equivalent to OH, and consequently to H, and if we replace both the hydrogens in water by this radicle we shall obtain $(SO_3H)_2O$—that is, pyrosulphuric acid.

hydrates of phosphoric acid (for example, PHO_3, $H_4P_2O_7$) have, even in aqueous solution, independent reactions which distinguish them and their salts from the perfect hydrates.

Sulphuric acid, H_2SO_4, is formed by the combination of its anhydride, SO_3, and water, with the evolution of a large amount of heat; the reaction $SO_3 + H_2O$ develops 21,300 heat units. The method of its preparation on a large scale and most of the methods employed for its formation are dependent on the oxidation of sulphurous anhydride and the formation of sulphuric anhydride, which forms sulphuric acid under the action of water. The technical method of its manufacture in lead chambers has been described in Chap. VI. The acid obtained **from the lead chambers** contains a considerable amount of water, and is also impure owing to the presence of oxides of nitrogen, lead compounds, and certain impurities from the burnt sulphur which have come over in a gaseous and vaporous state (for example, arsenic compounds). For practical purposes, hardly any notice is taken of the majority of these impurities, because they do not interfere with the ordinary properties. Most frequently, endeavours are only made to remove, as far as possible, all the water which can be expelled.[45] That is, the object is to obtain the hydrate, H_2SO_4, from the dilute acid (60 per cent.), and this is effected by evaporation by means of heat.

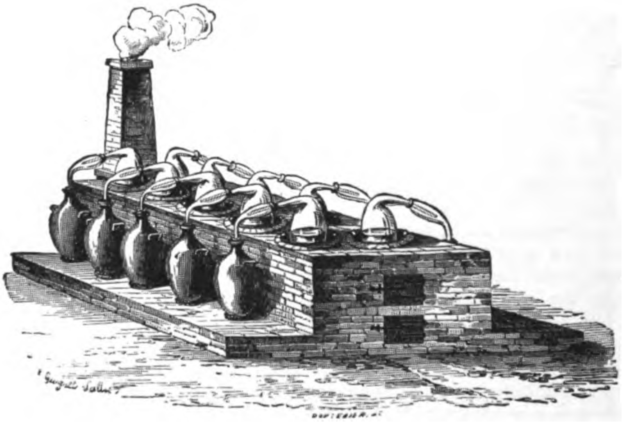


FIG. 98.—Concentration of sulphuric acid in glass retorts. The neck of each retort is attached to a bent glass tube, whose vertical arm is lowered into a glass or earthenware vessel acting as a receiver for the steam which comes over from the acid, as the former still contains a certain amount of acid.

---

[45] The removal of the water, or concentration to almost the real acid, H_2SO_4, is effected for two reasons: in the first place to avoid the expense of transit and in the second place because many processes—for instance, the refining of petroleum—require a strong acid free from an excess of water, the weak acid having no action.

All the aqueous solutions of sulphuric acid begin to part with a certain amount of aqueous vapour when heated to a certain definite temperature. At a low temperature either there is no evaporation of water, or there can even be an absorption of moisture from the air. As the removal of the water proceeds, the vapour pressure of the residue decreases for the same temperature, and therefore the more dilute the acid the lower the temperature at which it gives up a portion of its water. In consequence of this, the removal of water from dilute solutions of sulphuric acid may be easily carried on (up to 75 per cent. H_2SO_4) in lead vessels, because at low temperatures dilute sulphuric acid does not attack lead. But as the acid becomes more concentrated the temperature at which the water comes over becomes higher and higher, and then the acid begins to act on lead (with the evolution of sulphuretted hydrogen and conversion of the lead into sulphate), and therefore lead vessels cannot be employed for the complete removal of the water. For this purpose the evaporation is generally carried on in glass or platinum retorts, like those depicted in figs. 98 and 99.

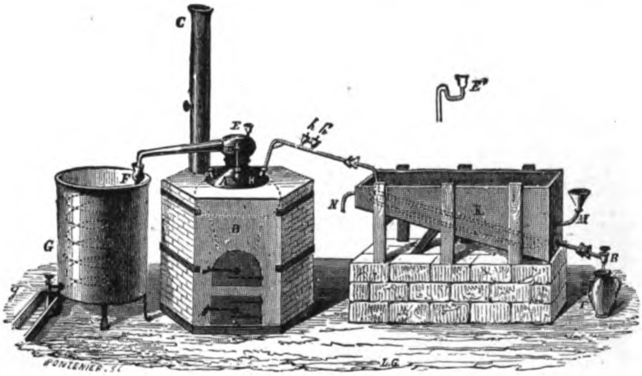


FIG. 99.—Concentration of sulphuric acid in platinum retorts.

The concentration of sulphuric acid in glass retorts is not a continuous process, and consists of heating the dilute 75 per cent. acid until it ceases to give off aqueous vapour, and until acid containing 93–98 per cent. H_2SO_4 is obtained—and this takes place when the temperature reaches 320° and the density of the residue attains a value 1·847 (66° Baumé).[46] The platinum vessels designed for the continuous

---

[46] The difficulty which which the last portions of water are removed is seen from the fact that the boiling becomes very irregular, totally ceasing at one moment, then suddenly starting again, with the rapid formation of a considerable amount of steam, and at the same time bumping and even overturning the vessel in which it is held. Hence it is not a rare occurrence for the glass retorts to break during the distillation; this causes platinum retorts to be preferred, as the boiling then proceeds quite uniformly.

concentration of sulphuric acid consist of a still B, furnished with a still head E, a connecting pipe E F, and a syphon tube H R, which draws off the sulphuric acid concentrated in the boiler. A stream of sulphuric acid previously concentrated in lead retorts to a density of about 60° Baumé—i.e., to 75 per cent. or a sp. gr. of 1·7—runs continuously into the retort through a syphon funnel E. The apparatus is fed from above, because the acid freshly supplied is lighter than that which has already lost water, and also because the water is more easily evaporated from the freshly supplied acid at the surface. The platinum retort is heated, and the steam coming off[47] is condensed in a worm F G, while as fresh dilute acid is supplied to the boiler, the acid already concentrated is drawn off through the syphon tube H B, which is furnished with a regulating cock by means of which the outflow of the concentrated acid from the bottom of the retort can be so regulated that it will always present one and the same specific gravity, corresponding with the strength required. For this purpose the acid flowing from the syphon is collected in a receiver, R, in which a hydrometer, indicating its density, floats; if its density is less than 66° Baumé, the regulating cock is closed sufficiently to retard the outflow of sulphuric acid, so as to lengthen the time of its evaporation in the retort.[48]

---

[47] According to Regnault, the vapour pressures (in millimetres of mercury) of the water given off by the hydrates of sulphuric acid, H_2SO_4,nH_2O, are—

	$t=5°$	15°	30°
$n=1$	0·1	0·1	0·2
2	0·4	0·7	1·5
3	0·9	1·6	4·1
4	1·3	2·8	7·0
5	2·1	4·2	10·7
7	3·2	6·2	15·6
9	4·1	8·0	19·6
11	4·4	9·0	22·2
17	5·5	10·6	26·1

With 89–98·6 per cent. H_2SO_4 the vapour pressure of the water is not observable even at 100° (Knitsch). The boiling-point under the atmospheric pressure, i.e., the temperature of evolution of aqueous vapour, rises with the amount of H_2SO_4, and for 98·5 per cent. acid is 317°. If the strength of the acid is still greater, SO_3 is given off and the normal (100 per cent.) hydrate H_2SO_4 boils at 245° and the solution containing 26 per cent. of anhydride dissolved in H_2SO_4 boils at 125°.

According to Lunge, the vapour pressure of the aqueous vapour given off from solutions of sulphuric acid containing p per cent. of H_2SO_4, at $t°$, equals the barometric pressure—720 to 730 mm.:

$p=$	10	20	30	40	50	60	70	d0	85	90	95
$t=$	102°	105°	108°	114°	124°	141°	170°	207°	233°	262°	295°

The latter figures give the temperature at which water is easily expelled from solutions of sulphuric acid of different strengths. But the evaporation begins sooner, and concentration may be carried on at lower temperatures if a stream of air be passed through the acid. Kessler's process is based upon this (note 48).

[48] The greatest part of the sulphuric acid is used for purposes in which an acid having

The great bulk of the lead chambers in which the 60 per cent. sulphuric acid is made, the waste of nitric acid, and the necessity of further concentrating the acid to a content of 97 per cent. H_2SO_4 render the manufacture of sulphuric acid complicated and costly. The researches of Phillips (1831), Wöhler (1852), Winkler (1875), and others on the formation of sulphuric anhydride (from SO_2 and oxygen) by contact with platinum or the oxides of iron, chromium, &c. have therefore been made the starting-point for the manufacture of sulphuric acid by the **contact process.** These endeavours were only crowned with success at the very close of the last century, thanks to the working out of all the technical details of the process, chiefly by Knitsch (1899) at the chemical works at Ludwigshaven (near the Rhine). In 1900 the Baden Aniline and Soda Works prepared 116,000 tons of sulphuric acid by this process at a less cost than chamber acid. Just as in the chamber process, the raw material here consists of a mixture of air and the gases produced by roasting FeS_2, ZnS, PbS, and other metallic sulphides, and containing about 7½ per cent. of SO_2. The contact

---

a density of 60° Baumé is amply sufficient. Chamber acid has a density up to 1·57 or 50° to 51° Baumé; it contains about 35 per cent. of water. About 15 per cent. of this water can be removed in leaden stills, and nearly all the remainder may be expelled in glass or platinum vessels. Acid of 66° Baumé = 1·847, contains about 96 per cent. of the hydrate H_2SO_4. The density falls with a greater or less proportion of water, the maximum density corresponding with 97½ per cent. of the hydrate H_2SO_4. The concentration of H_2SO_4 in platinum retorts has the disadvantage that sulphuric acid, upwards of 90 per cent. in strength, does corrode platinum, although but slightly (a few grams per tens of tons of acid). The retorts therefore require repairing, and the cost of the platinum exceeds the price obtained for concentrating the acid from 90 per cent. to 98 per cent. This inconvenience has lately (1891, by Matthey) been eliminated by coating the inside of the platinum retorts with a thin (0·1 to 0·02 mm.) layer of gold which is 40 times less corroded by sulphuric acid than platinum. Négrier (1890) carries on the distillation in porcelain dishes, Blond by heating a thin platinum wire immersed in the acid by means of an electric current, but the most profitable methods are that of Kessler (1891) and others of the same kind which consist in passing hot air over sulphuric acid flowing in a thin stream in stone vessels, so that there is no boiling but only evaporation at moderate temperatures.

When, by evaporation of the water, sulphuric acid attains a density of 66° Baumé (sp. gr. 1·84), it is impossible to concentrate it further, because it then distils over unchanged. **The distillation of sulphuric acid** is not generally carried on on a large scale, but forms a laboratory process, employed when particularly pure acid is required. The distillation is effected either in platinum retorts furnished with corresponding condensers and receivers, or in glass retorts. In the latter case, great caution is necessary because the boiling of sulphuric acid itself is accompanied by even more violent jerks and greater irregularity than the evaporation of the last portions of water contained in the acid. Generally the heating is not effected from below, but at the sides of the retort. The evaporation then does not proceed in the whole mass, but only from the upper portions of the liquid, and therefore goes on much more quietly. The acid may also be made to boil quietly by surrounding the retort with good conductors of heat—for example, iron filings, or by immersing a bunch of platinum wires in the acid, as the bubbles of sulphuric acid vapour then form on the extremities of the wires.

material employed is platinised asbestos,[48a] which lasts for an indefinite time. It is *loosely* laid on perforated sheets attached to an upright support in vertical iron tubes through which the mixture of air and SO_2 is made to pass. Besides the presence of an excess of oxygen a temperature of about 380° to 450° is necessary for the complete and rapid conversion of SO_2 into SO_3. The reaction proceeds slowly at a lower temperature, while a considerable amount of the SO_3 formed is decomposed at a higher temperature as the reaction, $SO_2+O=SO_3$, is reversible and evolves heat (see above). Hence the application of heat is only requisite at the beginning, while afterwards it may even be necessary to cool the tubes with water, should the temperature rise above 450°. The resultant SO_3 is absorbed (from its admixture with nitrogen and excess of oxygen) by water, or, better still, by sulphuric acid. In this manner a strong acid (98 per cent. H_2SO_4) or the anhydride itself may be obtained direct without the necessity of concentration. It is therefore extremely probable that this process will in time quite oust the chamber process, owing to its cheapness and simplicity.[48b]

Strictly speaking, **sulphuric acid is not volatile,** and at its so-called boiling-point it really decomposes into its anhydride and water, its boiling-point (338°) being nothing else than its temperature of decomposition. The products of this decomposition are substances boiling much below the temperature of the decomposition of sulphuric acid. This conclusion with regard to the process of the distillation of sulphuric acid may be deduced from Bineau's observations on the vapour density of sulphuric acid. This density referred to hydrogen proved to be half that which sulphuric acid should have according to its molecular weight, H_2SO_4, namely 49, the observed density being 24·5. Besides

---

[48a] The asbestos fibre is first immersed in a solution of $PtCl_4$ and then in one of NH_4Cl. A precipitate containing platinum is thus deposited on the fibres which are then dried and calcined. This leaves a coating of platinum black or finely divided platinum (about 4 per cent. by weight) on the fibres, which renders them catalytic. The platinised asbestos soon loses its power if the gases acting on it contain any traces of arsenic or mercury, as the latter settle on the platinum. And as pyrites always contain some arsenic, the gases obtained from roasting them have first to be very carefully mixed (by means of a jet of steam), cooled and washed in water and sulphuric acid. This apparently trivial fact for a long time prevented the contact method from being profitable.

It should be remembered that the oxides of nitrogen also serve as a contact substance in the chamber process, just like platinum in the present case, only the latter is solid and non-volatile, whereas the oxides of nitrogen are gaseous and therefore easily lost.

[48b] Strong 98 per cent. sulphuric acid may be conveniently kept in cast-iron vessels, but the fuming acid cannot, because they crack after a time. This is probably due to the presence of cavities in the cast iron in which gases, produced by the SO_3 acting upon the iron, accumulate and produce pressure and rupture. Forged iron vessels are therefore used for keeping this kind of acid.

which, Marignac showed that the first portions of the sulphuric acid distilling over contain less of the elements of water than the portion which remains behind, or which distils over towards the end. This is explained by the fact that on distillation the sulphuric acid is decomposed, but a portion of the water proceeding from its decomposition is retained by the remaining mass of sulphuric acid, and therefore at first a mixture of sulphuric acid and sulphuric anhydride—i.e., fuming sulphuric acid—is obtained in the distillate. It is possible by repeating the distillation several times and only collecting the first portions of the distillate to obtain a distinctly fuming acid. To obtain the definite hydrate H_2SO_4, it is necessary to refrigerate a highly concentrated acid, of as great a purity as possible, to which a small quantity of sulphuric anhydride has been previously added. Sulphuric acid containing a small quantity (a fraction of a per cent. by weight) of water only freezes at a very low temperature, while the pure normal acid, H_2SO_4, solidifies when it is cooled below 0°, and therefore the normal acid first crystallises out from the concentrated sulphuric acid. By repeating the refrigeration several times, and pouring off the unsolidified portion, it is possible to obtain a pure **normal hydrate,** H_2SO_4, which melts at 10·4°. Even at 40° it gives off distinct fumes—that is, it begins to evolve sulphuric anhydride, and therefore even in a dry atmosphere the hydrate H_2SO_4 becomes weaker, until it contains 98½ per cent. H_2SO_4 and 1½ of water.[49]

---

[49] Thus it appears that so common, and apparently so stable, a compound as sulphuric acid decomposes even at a low temperature with separation of the anhydride, but this decomposition is restricted by a limit, corresponding to the presence of about 1½ per cent. of water, or to a composition of nearly $H_2O,12H_2SO_4$.

Now there is no reason for thinking that this substance is a definite compound; it is an equilibrated system which does not decompose, under ordinary circumstances, below 338°. Dittmar carried on the distillation under pressures varying between 30 and 2,140 millimetres (of mercury), and he found that the composition of the residue hardly varies, and contains from 99·2 to 98·2 per cent. of the normal hydrate, although at 30 mm. the temperature of distillation is about 210° and at 2,140 mm. it is 382°. Furthermore, it is a fact of practical importance that under a pressure of two atmospheres the distillation of sulphuric acid proceeds very quietly.

Sulphuric acid may be **purified** from the majority of its impurities by distillation, if the first and last portions of the distillate be rejected. The first portions will contain the oxides of nitrogen, hydrochloric acid, &c., and the last portions the less volatile impurities. The oxides of nitrogen may be removed by heating the acid with charcoal, which converts them into volatile gases. Sulphuric acid may be freed from arsenic by heating it with manganese dioxide and then distilling. This oxidises all the arsenic into non-volatile arsenic acid. Without a preliminary oxidation it would partially remain as volatile arsenious acid, and might pass over into the distillate. The arsenic may also be driven off by first reducing it to arsenious acid, and then passing hydrochloric acid gas through the heated acid. It is then converted into arsenious chloride, which volatilises. Chamber acid always contains arsenic, but that prepared by the contact method (note 48a) is usually free from arsenic.

In a concentrated form sulphuric acid is commercially known as **oil of vitriol,** because for a long time it was obtained from green vitriol and has an oily appearance. When mixed with water, sulphuric acid develops a very considerable amount of heat.[50]

Besides the normal hydrate, H_2SO_4, **another definite hydrate,** H_2SO_4,H_2O (84·48 per cent. of the normal hydrate, and 15·52 per cent. of water) is known; it crystallises[50a] extremely easily in large six-

---

[50] The amount of heat developed by the mixture of sulphuric acid with water is expressed in the diagram on p. 74, Volume I., by the middle curve, the abscissæ being the percentage amounts of acid (H_2SO_4) in the resultant solution, and the ordinates the numbers of units of heat corresponding with the formation of 100 cubic centimetres of the solution (at 18°). The calculations on which the curve is designed are based on Thomsen's determinations, which show that 98 grams or a molecular amount of sulphuric acid, in combining with m molecules of water (that is, with $m \times 18$ grams of water), develop the following number of units of heat, R:—

$m =$	1	2	3	5	9	19	49	100	200
R =	6379	9418	11137	13108	14952	16256	16684	16859	17066
c =	0·432	0·470	0·500	0·576	0·701	0·821	0·914	0·954	0·975
T =	127°	149°	146°	121°	82°	45°	19°	9°	5°

c representing the specific heat of $H_2SO_4mH_2O$ (according to Marignac and Pfaundler), and T the rise in temperature which proceeds from the mixture of H_2SO_4 with mH_2O. The diagram shows that contraction and rise of temperature proceed almost parallel with each other.

[50a] Pickering (1890) showed (*a*) that dilute solutions of sulphuric acid containing up to $H_2SO_4 + 10H_2O$ deposit ice at −0·12° when there is $2000H_2O$ per H_2SO_4, at −0·23° when there is $1000H_2O$, at −1·04° when there is $200H_2O$, at −2·12° when there is $100H_2O$, at −4·5° when there is $50H_2O$, at −15·7° when there is $20H_2O$, and at −61° when the composition of the solution is $H_2SO_4 + 10H_2O$; (*b*) that for higher concentrations crystals separate out at a considerable degree of cold, having the composition $H_2SO_4,4H_2O$, and melting at −24·5°, and if either water or H_2SO_4 is added to this compound the temperature of crystallisation falls, so that a solution of the composition $12H_2SO_4 + 100H_2O$ gives crystals of the above hydrate at −70°, $15H_2SO_4 + 100H_2O$ at −47°, $30H_2SO_4 + 100H_2O$ at −32°, $40H_2SO_4 + 100H_2O$ at −52°; (*c*) that if the amount of H_2SO_4 is still greater, a hydrate H_2SO_4,H_2O separates out and melts at +8·5°, while the addition of water or sulphuric acid to it lowers the temperature of crystallisation, so that the crystallisation of H_2SO_4,H_2O from a solution of the composition $H_2SO_4 + 1{\cdot}78H_2O$ takes place at −22°, from $H_2SO_4 + 1{\cdot}5H_2O$ at −6·5°, $H_2SO_4 + 1{\cdot}2H_2O$ at +3·7°, $H_2SO_4 + 0{\cdot}75H_2O$ at +2·8°, $H_2SO_4 + 0{\cdot}5H_2O$ at −16°; (*d*) that when there is less than $40H_2O$ per $100H_2SO_4$, refrigeration separates out the normal hydrate H_2SO_4, which melts at +10·35°, and that a solution of the composition $H_2SO_4 + 0{\cdot}35H_2O$ deposits crystals of this hydrate at −34°, $H_2SO_4 + 0{\cdot}10H_2O$ at −4·1°, $H_2SO_4 + 0{\cdot}05H_2O$ at +4·9°, while fuming acid of the composition $H_2SO_4 + 0{\cdot}05SO_3$ deposits H_2SO_4 at about +7°. Thus, the temperature of the separation of crystals clearly distinguishes the above four regions of solutions, and in the space between $H_2SO_4 + H_2O$ and $+25H_2O$, there separates out a particular hydrate, $H_2SO_4,4H_2O$ (discovered by Pickering), the isolation of which deserves full attention and further research. I may add here that the existence of a hydrate $H_2SO_4,4H_2O$ was pointed out in my work, *The Investigation of Aqueous Solutions*, p. 120 (1887), upon the basis that it has at all temperatures a smaller value for the coefficient of expansion, k, in the formula, $S_t = S_0(1-kt)$, than the adjacent (in composition) solutions of sulphuric acid. And for solutions approximating to $H_2SO_4,10H_2O$ in their composition, k is constant at all temperatures (for more dilute solutions the value of k increases with t and for more concentrated solutions it decreases). This solution (with $10H_2O$) forms the point of transition between more dilute solutions

sided prisms, which form above 0°—namely, at about +8·5°; when heated at 210° it loses water.[51] If the hydrates H_2SO_4 and H_2SO_4,H_2O exist at low temperatures as definite crystalline compounds, and if pyrosulphuric acid, H_2SO_4,SO_3, has the same property, and if they all decompose with more or less ease on a rise of temperature, with the disengagement of either SO_3 or H_2O, and in their ordinary form present all the properties of simple solutions, it follows that between sulphuric anhydride, SO_3, and water, H_2O, there exists a consecutive series of homogeneous liquids or solutions, among which we must distinguish *definite compounds*, and therefore it is quite justifiable to look for other definite compounds between SO_3 and H_2O, beyond the conditions for a change of state. In this respect we may be guided by the variation of properties of any kind, proceeding concurrently with a variation in the composition of a solution.

---

which deposit ice (water) when refrigerated and those which give crystals of $H_2SO_4,4H_2O$. The researches of Knitsch (1901) on the melting-points of strong and fuming sulphuric acids show that there are four maxima alternated by three minima between H_2SO_4,H_2O and SO_3, and namely:—

Composition	Melting-point
H_2SO_4,H_2O	+ 8° (max.)
$(H_2SO_4)_2,H_2O$	−35° (min.)
H_2SO_4	+10° (max.)
$SO_3,(H_2SO_4)_4$	−11° (min.)
$SO_3,(H_2SO_4)$	+34° (max.)
$(SO_3)_2,H_2SO_4$	−0·8° (min.)
SO_3 (polymerised)	+40° (max.)

Definite compounds are now supposed by many to correspond to the higher temperatures only, whilst the lower temperatures belong to eutectic mixtures (see Chap. I., note 58). But here, as in many other cases (especially with metallic alloys), these points correspond to substances having a definite molecular (simple) composition. I therefore hold that a strictly definite composition and simple relation in the number of molecules, similar to those of true definite compounds, correspond in many, if not all, cases to the eutectic points. The reason for this must be sought in the dependence of all physico-mechanical properties on those forces and relations which are determined by chemical reaction—i.e., on the mass of the reacting chemical particles. If anywhere between two definite compounds having a maximum t there lies a composition with a minimum t, it may, I think, be most readily explained by some simple relation between the number of particles of the component substances, for all their properties must be connected with their molecular weight. Such is the spirit of all chemical doctrines since the establishment of the conceptions of atoms, molecules, periodicity, &c. The phenomena exhibited between water and sulphuric acid should be kept in mind in the investigation of solutions and alloys. Everything is not clear even here, but still there is much that is clearer than in other solutions or in alloys.

[51] With an excess of snow, the hydrate H_2SO_4,H_2O, like the normal hydrate, gives a freezing mixture, owing to the absorption of a large amount of heat (the latent heat of fusion). In melting, the molecule H_2SO_4 absorbs 960 heat units, and the molecule H_2SO_4,H_2O, 3,680 heat units. If therefore we mix one gram molecule of this hydrate with seventeen gram molecules of snow, there is an absorption of 18,080 heat units, because $17H_2O$ absorbs 17 × 1,430 heat units, and the combination of the monohydrate with water evolves 9,800 heat units. As the specific heat of the resultant compound $H_2SO_4,18H_2O$ is 0·813, the fall of temperature will be 52·6°. And in fact a very low temperature may be obtained by means of sulphuric acid.

But only a few properties have been determined with sufficient accuracy. In those properties which have been determined for many solutions of sulphuric acid, it is actually seen that the above-mentioned definite compounds are distinguished by distinctive marks of change. As an example we may cite the variation of the specific gravity with a variation of temperature (namely, $K = ds/dt$, if s be the sp. gr. and t the temperature). For the normal hydrate, H_2SO_4, this factor is easily determined from the fact that

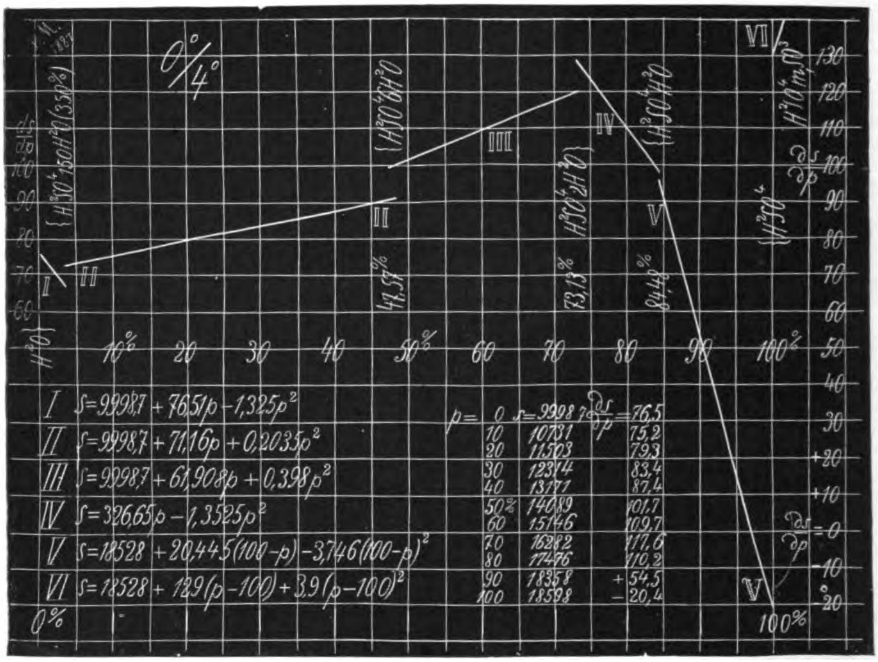


FIG. 100.—Diagram showing the variation of the factor (ds/dp) of the specific gravity of solutions of sulphuric acid. The percentage quantities of the acid, H_2SO_4, are laid out on the axes of abscissæ. The ordinates are the factors or rises in sp. gr. (water at 4° = 10,000) with the increase in the quantity of H_2SO_4.

$$s = 18528 - 10{\cdot}65t + 0{\cdot}013t^2,$$

where s is the specific gravity at t (degrees Celsius), the sp. gr. of water at 4° being 10,000. Therefore $K = 10{\cdot}65 - 0{\cdot}026t$. This means that at 0° the sp. gr. of the acid H_2SO_4 decreases by 10·65 for every rise of a degree of temperature, at 10° by 10·39, at 20° by 10·13, and at 30° by 9·87.[52] And for solutions containing slightly more anhydride than the

---

[52] For example, if it be taken that at 19° the sp. gr. of pure sulphuric acid is 1·8330, at 20° it will be 1·8330 − (20 − 19)10·13 = 1·8320.

acid H_2SO_4 (i.e., for fuming sulphuric acid), as well as for solutions containing more water, K is greater than for the acid H_2SO_4. Thus, for the solution $SO_3,2H_2SO_4$ at 10°, K=11·0. On diluting the acid H_2SO_4, K again increases until the formation of the solution H_2SO_4,H_2O (for which K=11·1 at 10°), and then, on further dilution with water, it again decreases. Consequently both the hydrates H_2SO_4 and H_2SO_4,H_2O are here expressed by an alteration of the magnitude of K.

This shows that in solutions it is possible, by studying the variation of their properties (without a change of physical state), to recognise the presence or formation of definite hydrate compounds, and therefore an exact investigation of the properties of solutions, of their specific gravity for instance, should give direct indications of such compounds.[53] The mean result of the most trustworthy determinations of this nature is given in the following tables. The first of these tables gives the specific gravities (*in vacuo*, taking the sp. gr. of water at 4° as 1), at 0°, 15° and 30°,[53a] for solutions having the composition $H_2SO_4+nH_2O$ (the value of n is given in the first column), and contains p (column 2) per cent. (by weight *in vacuo*) of H_2SO_4.

n	p	0°	15°	30°
100	5·16	1·0374	1·0341	1·0292
50	9·82	1·0717	1·0666	1·0603
25	17·88	1·1337	1·1257	1·1173
15	26·63	1·2040	1·1939	1·1837
10	35·25	1·2758	1·2649	1·2540
8	40·50	1·3223	1·3110	1·2998
6	47·57	1·3865	1·3748	1·3632
5	52·13	1·4301	1·4180	1·4062
4	57·65	1·4881	1·4755	1·4631
3	64·47	1·5635	1·5501	1·5370
2	73·13	1·6648	1·6500	1·6359
1	84·48	1·7940	1·7772	1·7608
0·5	91·59	1·8445	1·8284	1·8128
H_2SO_4	100	1·8529	1·8372	1·8221

---

[53] Unfortunately, notwithstanding the great number of fragmentary and systematic researches which have been made (by Parkes, Ure, Bineau, Kolbe, Lunge, Marignac, Kremers, Thomsen, Perkin, and others) for determining the relation between the sp. gr. and composition of solutions of sulphuric acid, they contain discrepancies which amount to, and even exceed, 0·002 in the sp. gr. For instance, at 15·4° the solution of composition $H_2SO_4,3H_2O$ has a sp. gr. 1·5493 according to Perkin (1886), 1·5501 according to Pickering (1890), and 1·5525 according to Lunge (1890). So that the specific gravities given in the adjoining tables are only the average and most probable data in which the error, especially for the 30–80 per cent. solutions, may be not less than 0·0010 (taking water at 4° as 1)

[53a] Judging from the best existing determinations (of Marignac, Kremers, and Pickering) for solutions of sulphuric acid (especially those containing more than 5 per cent.

In the second table the first column gives the percentage amount p (by weight) of H_2SO_4; the second, the weight in grams (S_{15}) of a litre of the solution at 15° (at 4° the weight of a litre of water is 1000 grams); the third, the variation (dS/dt) of this weight for a rise of 1°; the fourth, the variation dS/dp of this weight (at 15°) for a rise of 1 per cent. of H_2SO_4; the fifth, the difference between the weight of a litre at 0° and 15° (S_0-S_{15}), and the sixth column, the difference between the weight of a litre at 15° and 30° ($S_{15}-S_{30}$).

p	S_{15}	dS_{15}/dt	dS_{15}/dp	S_0-S_{15}	$S_{15}-S_{30}$
0	999·15	0·148	7·0	0·7	3·4
5	1033·0	0·27	6·8	3·1	5·0
10	1067·7	0·38	7·1	5·2	6·4
20	1141·9	0·58	7·7	8·6	8·9
30	1221·3	0·69	8·2	10·4	10·4
40	1306·6	0·75	8·8	11·3	11·2
50	1397·9	0·79	9·9	11·9	11·8
60	1501·2	0·86	10·8	13·0	12·7
70	1613·1	0·93	11·6	14·1	13·8
80	1731·4	1·04	11·0	15·8	15·4
90	1819·9	1·08	5·4	16·4	16·0
95	1837·6	1·03	+1·7	15·8	15·1
100	1837·2	1·03	−1·9[54]	15·7	15·1

The figures in these tables give the means of finding the amount of H_2SO_4 contained in a solution from its specific gravity,[55] and also

---

of H_2SO_4) within the limits of 0° and 30° (and even to 40°), the variation of the sp. gr. with the temperature, t, may (within the accuracy of the existing determinations) be perfectly expressed by the equation: $S_t = S_0 + At + Bt^2$. It must be added that (1) three specific gravities fully determine the variation of the density with t; (2) $ds/dt = A + 2Bt$, i.e., the factor of the temperature is expressed by a straight line; (3) the value of A (if p is greater than 5 per cent.) is negative, and numerically much greater than B; (4) the value of B for dilute solutions containing less than 25 per cent. is negative; for solutions approximating to $H_2SO_4,3H_2O$ in their composition it is equal to 0, and for solutions of greater concentration B is positive; (5) the factor ds/dp for all temperatures attains a maximum value about H_2SO_4,H_2O; (6) on dividing ds/dt by S_0, and so obtaining the coefficient of expansion k (see note 53), a minimum is obtained near H_2SO_4 and $H_2SO_4,4H_2O$, and a maximum at H_2SO_4,H_2O for all temperatures.

[54] The factor ds/dp passes through 0, that is, the specific gravity attains a maximum value at about 98 per cent. This was discovered by Kohlrausch, and confirmed by Chertel, Pickering, and others.

[55] Naturally under the condition that there is no other ingredient besides water, which is sufficiently true. For commercial acid, whose specific gravity is usually expressed in degrees of Baumé's hydrometer, we may add that at 15°—

Specific gravity	1	1·1	1·2	1·3	1·4	1·5	1·6	1·7	1·8
Degree Baumé	0	13	24	33·3	41·2	48·1	54·1	59·5	64·2

66° Baumé (the strongest commercial acid or oil of vitriol) corresponds to a sp. gr. 1·84. By employing the second table (by the method of interpolation) the specific gravity show that 'special points' in the lines of variation of the specific gravity with the temperature and percentage composition correspond with certain definite compounds of H_2SO_4 with OH_2. This is best seen in the variation of the factors (dS/dt and dS/dp) with the temperature and composition (columns 3, 4, second table). The factor dS/dp (giving the increase of sp. gr. with an increase of 1 per cent. H_2SO_4) points to the following three facts : (1) In passing from 98 per cent. to 100 per cent. acid the factor is negative, and is at 100 per cent. about $-0{\cdot}0019$ (i.e., at 99 per cent. the sp. gr. at 15° is about 1·8391, and at 100 per cent. about 1·8372, the amount of H_2SO_4 having increased while the sp. gr. has decreased), but as soon as a certain amount of SO_3 is added to the definite compound H_2SO_4 (and 'fuming' acid formed) the specific gravity rises (for example, for $H_2SO_4, 0{\cdot}136\,SO_3$, the sp. gr. at 15° is 1·866), that is, the factor becomes positive (and, in fact, greater by $+0{\cdot}01$), so that the formation of the definite hydrate H_2SO_4 is accompanied by a distinct and considerable break in the continuity of the factor;[55a] (2) the factor dS/dp, in increasing in its passage from dilute to concentrated solutions, attains a maximum value (at 15°, about 0·012) at about $H_2SO_4,2H_2O$, i.e., at about the hydrate corresponding to the form SX_6 proper to the compounds of sulphur, for $S(OH)_6=H_2SO_4,2H_2O$; the same hydrate corresponds to the composition of gypsum, $CaSO_4,2H_2O$, and to it also corresponds the greatest contraction and rise of temperature in mixing H_2SO_4 with H_2O (see Chap. I., note 28); (3) the variation of the factor dS/dp, under certain variations in the composition, proceeds so uniformly and regularly, and is so different from the variation given under other proportions of H_2SO_4 and H_2O, that the sum of the variations of dS/dp is expressed by a series of straight lines, if the values of p be laid along the axis of abscissæ and those of dS/dp along the ordinates.[56]

---

at a given temperature (from 0° to 30°) can be found for any percentage amount of H_2SO_4, and therefore conversely the percentage of H_2SO_4 can be found from the specific gravity.

[55a] Whether similar (even small) breaks in the continuity of the factor ds/dp exist or not, for other hydrates (for instance, for H_2SO_4,H_2O and $H_2SO_4,4H_2O$) cannot as yet be affirmed, owing to the want of accurate data (note 53). In my investigation of this subject (1887) I admit their possibility, but only conditionally; and now, without insisting upon a similar opinion, I only hold to the existence of a distinct break in the factor at H_2SO_4, being guided by C. Winkler's observations on the specific gravities of fuming sulphuric acid.

[56] In 1887, on considering all the existing observations for a temperature 0°, I gave a full scheme of the variation of the factor ds/dp at 0°.

I did not then (1887) give this scheme an absolute value, and now after the appearance of two series of new determinations (Lunge and Pickering in 1890), which disagree in many points, I think it well to state quite clearly that Lunge's and Pickering's new determinations have not added to the accuracy of our data respecting the variation of the sp. gr. of solutions of sulphuric acid, and that this subject deserves (as I mentioned

Thus, for instance, for 15°, at 10 per cent., $dS/dp=0{\cdot}0071$; at 20 per cent., 0·0077; at 30 per cent., 0·0082; and at 40 per cent., 0·0088; that is, for each 10 per cent. the factor increases by about 0·0006 for the whole of the above range, but beyond this it becomes larger, and then, after passing $H_2SO_4,2H_2O$, it begins to fall rapidly. Such changes in the variation of the factor apparently take place at about definite hydrates,[56a] and especially about $H_2SO_4,4H_2O$, $H_2SO_4,2H_2O$ and H_2SO_4,H_2O. All this, indicating as it does the special chemical affinity of sulphuric acid for water, although of no small significance for comprehending the nature of solutions (see Chap. I. and Chap. VII.), contains many special points which require detailed investigation, the chief difficulty being that it requires great accuracy in a large number of experimental data.

The great affinity of sulphuric acid for water is also seen from the fact that when the strong acid acts on the majority of organic substances containing hydrogen and oxygen (especially on heating) it very frequently takes up these elements in the form of water. Thus strong sulphuric acid, acting on alcohol, C_2H_6O, removes the elements of water from it, and converts it into olefiant gas, C_2H_4. It acts in a similar manner on wood and other vegetable tissues, which it **chars.** If a piece of wood is immersed in strong sulphuric acid it turns black. This is owing to the fact that the wood contains carbohydrates, for example, cellulose, $C_6H_{10}O_5$, which give up hydrogen and oxygen as water to the sulphuric acid, leaving charcoal, or a black mass very rich in it.[57]

We have already had frequent occasion to notice the very

in 1887) new and careful elaboration, because it concerns that foremost problem in our science—solutions—and introduces a special method into it—that is, the study of differential variations in a property which is so easily observed as the specific gravity of a liquid.

[56a] H. Crompton (1888), in his researches on the electrical conductivity of solutions of sulphuric acid, and Tammann, in his observations on their vapour pressure, and Kouriloff (1891), in studying the formation of peroxide of hydrogen in the electrolysis of solutions of sulphuric acid, found a correlation with the hydrates indicated as above by the investigation of their specific gravities. Still, the whole question is so complicated, and the experimental data as yet so imperfect, that neither the number nor exact composition of many hydrates can be considered quite certain.

[57] Cellulose, for instance, unsized paper or calico, is dissolved by strong sulphuric acid. Acid diluted with about half its volume of water converts it (if the action be of short duration) into vegetable parchment (Chap. I., note 18). The action of dilute solutions of sulphuric acid converts it into hydro-cellulose, and the fibre loses its coherent quality and becomes brittle. The prolonged action of strong sulphuric acid chars the cellulose, while dilute acid converts it into glucose. If sulphuric acid be kept in an open vessel, the organic matter of the dust held in the atmosphere falls into it and blackens the acid. It is evident from the preceding that strong sulphuric acid will act as a powerful poison; whilst, on the other hand, when very dilute, it is employed in certain medicines and as a fertiliser for plants.

energetic acid properties of sulphuric acid, so that we shall now only consider a few of their aspects. First of all, we must remember that, with calcium, strontium, and especially with barium and lead, sulphuric acid forms very slightly soluble salts, whilst with the majority of other metals it gives more easily soluble salts, which in the majority of cases are able, like sulphuric acid itself, to combine with water to form crystallo-hydrates. Normal sulphuric acid, containing two atoms of hydrogen in its molecule, is able for this reason alone to form two classes of salts, **normal** and **acid**, which it does with great facility **with the alkali metals.** The metals of the alkaline earths and the majority of other metals, if they do form acid sulphates, only do so under exceptional conditions (with an excess of strong sulphuric acid), and these salts when formed are decomposable by water—that is, although having a certain degree of physical stability they have no chemical stability. Besides the acid salts, $RHSO_4$, sulphuric acid also gives other forms of acid salts. An entire series of salts having the composition $RHSO_4,H_2SO_4$, or for bivalent metals $RSO_4,3H_2SO_4$,[58] has been prepared. Such salts have been obtained for potassium, sodium, nickel, calcium, silver, magnesium, and manganese. They are prepared by dissolving the sulphates in an excess of sulphuric acid and heating the solution until the excess of acid is driven off; on cooling, the mass solidifies to a crystalline salt. Besides which, Rose obtained a salt having the composition $Na_2SO_4,NaHSO_4$, and if $HNaSO_4$ is heated it easily forms a salt, $Na_2S_2O_7 = Na_2SO_4,SO_3$; hence it is clear that sulphuric anhydride combines with various proportions of bases, just as it combines with various proportions of water.

We have already learned that sulphuric acid displaces the acid from the salts of nitric, carbonic, and many other volatile acids. Berthollet's laws (Chap. X.) explain this by the small volatility of sulphuric acid; and, indeed, in aqueous solution sulphuric acid displaces the much less soluble boric acid from its compounds; for instance, from borax, and it also displaces silica from its compounds with bases; but both boric anhydride and silica, when fused with sulphates, decompose them, displacing sulphuric anhydride, SO_3, because they are less volatile than sulphuric anhydride. It is also well known that with metals, sulphuric acid forms salts, hydrogen (with Fe, Zn, &c.) or sulphur dioxide (with Cu, Hg, &c.) being evolved.[58a]

---

[58] Weber (1884) obtained a series of salts, $R_2O,8SO_3,nH_2O$ for K, Rb, Cs, and Tl.

[58a] Ditte (1890) divides all the metals into two groups with respect to their behaviour with sulphuric acid: the first group includes silver, mercury, copper, lead, and bismuth, which are only acted upon by hot concentrated acid. In this case sulphurous anhydride is evolved without any by-reactions. The second group contains manganese, nickel, cobalt, iron, zinc, cadmium, aluminium, tin, thallium, and the alkali metals. They react with

The reactions of sulphuric acid **with respect to organic substances** are generally determined by its acid character, when neither the direct extraction of water, nor oxidation at the expense of the oxygen of the sulphuric acid,[59] nor disintegration takes place. Thus the majority of the unsaturated hydrocarbons, C_nH_{2m}, form with sulphuric acid a special class of **sulphonic acids**, $C_nH_{2m-1}(HSO_3)$; for example, benzene, C_6H_6, forms benzenesulphonic acid, $C_6H_5{\cdot}SO_3H$. It is evident from the existence of these acids that the hydrogen in organic compounds is replaceable by the group SO_3H, just as it may be replaced by the radicles Cl, NO_2, CO_2H, and others. As the radicle of sulphuric acid or **sulphoxyl**, SO_2OH or SHO_3, contains, like carboxyl (Vol. I., p. 419), one hydrogen (as hydroxyl) of the sulphuric acid, the resultant substances are acids whose basicity is equal to the number of hydrogens replaced by sulphoxyl. Since also sulphoxyl takes the place of hydrogen, and itself contains hydrogen, the sulpho-acids are equal to a hydrocarbon $+SO_3$, just as every organic (carboxylic) acid is equal to a hydrocarbon $+CO_2$. As a matter of fact, many sulphonic acids are obtained by the direct combination of sulphuric anhydride: $C_6H_5(SO_3H)=C_6H_6+SO_3$. The sulphonic acids give soluble barium salts, and are therefore easily distinguished from sulphuric acid. They are soluble in water and non-volatile, and when distilled give sulphurous anhydride (whilst the hydroxyl previously in combination with the sulphurous anhydride remains in the hydrocarbon group; thus, phenol, $C_6H_5{\cdot}OH$, is obtained from benzenesulphonic acid), and they are very energetic, because the hydrogen acting in them is of the same nature as in sulphuric acid itself.[60]

---

sulphuric acid of any concentration at any temperature. At a low temperature, hydrogen is disengaged, and at higher temperatures (and with very concentrated acid), hydrogen and sulphurous anhydride are simultaneously evolved.

[59] For example, the action of hot sulphuric acid on nitrogenous compounds, as applied in Kjeldahl's method for the estimation of nitrogen (Volume I., p. 265). It is obvious that when sulphuric acid acts as an oxidising agent it forms sulphurous anhydride.

The action of sulphuric acid on the alcohols is exactly similar to its action on alkalies, because the alcohols, like alkalies, react with acids; a molecule of alcohol with a molecule of sulphuric acid gives off water and forms an *acid* ethereal salt—that is, there is produced an ethereal compound corresponding with acid salts. Thus, for example, the action of sulphuric acid, H_2SO_4, on ordinary alcohol, C_2H_5OH, gives water and sulphovinic acid, $C_2H_5HSO_4$—that is, sulphuric acid in which one atom of hydrogen is replaced by the radicle C_2H_5 of ethyl alcohol, $SO_2(OH)(OC_2H_5)$, or, what is the same thing, the hydrogen in alcohol is replaced by the radicle (sulphoxyl) of sulphuric acid, $C_2H_5O{\cdot}SO_2(OH)$.

[60] We shall mention the following difference between the sulphonic acids and the ethereal acid sulphates (note 59): the former re-form sulphuric acid with difficulty and the latter easily. Thus, sulphovinic acid when heated with an excess of water is reconverted into alcohol and sulphuric acid. This is explained in the following manner. Both these classes of acids are produced by the substitution of hydrogen by SO_3H, or the

Sulphuric acid, as containing a large proportion of oxygen, is a substance which frequently acts as an oxidising agent, in which case it is **deoxidised, forming sulphurous anhydride** and water (or even, although more rarely, sulphuretted hydrogen and sulphur). Sulphuric acid acts in this manner on charcoal, copper, mercury, silver, organic and other substances, which are unable to evolve hydrogen from it directly, as we saw in describing sulphurous anhydride.

Although the hydrate of a higher saline form of oxidation (Chap. XV.), sulphuric anhydride is capable of further oxidation, and forms a kind of peroxide, just as hydrogen gives hydrogen peroxide in addition to water, or as sodium and potassium, besides the oxides Na_2O and K_2O, give their peroxides, compounds which are in a chemical sense unstable, powerfully oxidising, and not directly able to enter into saline combinations. If the oxides of potassium, barium, &c., be compared with water, their peroxides must in like manner correspond to hydrogen peroxide,[61] not only because the oxygen contained in them is very mobile and easily liberated, and because their reactions are similar, but also because they can be mutually transformed into each other, and are able to form compounds with each other, with bases and with water, and indeed form a kind of peroxide salts.[62]

---

univalent radicle of sulphuric acid, but in the formation of ethereal acid sulphates the SO_3H replaces the hydrogen of the hydroxyl in the alcohol, whilst in the formation of the sulphonic acids the SO_3H replaces the hydrogen of a hydrocarbon. This difference is clearly evidenced in the existence of two acids of the composition $SO_4C_2H_6$. The one, mentioned above, is sulphovinic acid or alcohol, $C_2H_5{\cdot}OH$, in which the hydrogen of the hydroxyl is replaced by sulphoxyl $= C_2H_5{\cdot}OSO_3H$, whilst the other is alcohol, in which one atom of the hydrogen in ethyl, C_2H_5, is replaced by the sulphonic group—that is $= (C_2H_4)SO_3H{\cdot}OH$. The latter is called isethionic acid. It is more stable than sulphovinic acid. The details as to these interesting compounds must be looked for in works on organic chemistry, but I think it necessary to note one of the general methods of formation of these acids. The sulphites of the alkalies—for example, K_2SO_3—when heated with the halogen products of metalepsis, give a halogen salt and a salt of a sulphonic acid. Thus methyl iodide, CH_3I, derived from marsh gas, CH_4, when heated to 100° with a solution of potassium sulphite, K_2SO_3, gives potassium iodide, KI, and potassium methylsulphonate, CH_3SO_3K—that is, a salt of the sulphonic acid. This shows that the sulphonic acid may be referred to sulphurous acid, and that there is a resemblance between sulphuric and sulphurous acid, which is most simply expressed by the fact that in sulphuric acid the sulphoxyl is combined with OK, while in sulphurous acid it is combined with H, for $H_2SO_3 = H(HSO_3)$.

[61] The reaction $BaO + O$ develops 12,000 heat units, whilst the reaction $H_2O + O$ absorbs 21,000 heat units.

[62] Schöne obtained a compound of peroxide of barium with peroxide of hydrogen. If barium peroxide be dissolved in hydrochloric (or acetic) acid, or if a solution of hydrogen peroxide be diluted with a solution of barium hydroxide, a pure hydrate will be precipitated having the composition $BaO_2,8H_2O$ (sometimes the composition is taken as $BaO_2,6H_2O$). This fact was already known to Thénard. Schöne showed that if hydrogen peroxide is in excess, a crystalline compound of the two peroxides, BaO_2,H_2O_2, is precipitated. Thus, barium peroxide combines with both water and hydrogen peroxide. This is a very important fact for the comprehension of the composition of other peroxides.

This is also the character of **persulphuric acid**, discovered in 1878 by Berthelot, and its corresponding anhydride or **peroxide of sulphur**, S_2O_7. It is formed from $2SO_3+O$ with the absorption of heat (−27 thousand heat units), like ozone from O_2+O (−29 thousand units of heat), or hydrogen peroxide from $H_2O + O$ (− 21 thousand heat units).

Peroxide of sulphur is produced by the action of a silent discharge upon a mixture of oxygen and sulphurous anhydride.[63] With water S_2O_7 gives persulphuric acid, $H_2S_2O_8$. The latter is obtained more simply by mixing strong sulphuric acid (not weaker than $H_2SO_4,2H_2O$) directly with hydrogen peroxide, or by the action of a galvanic current on sulphuric acid mixed with a certain amount of water, and cooled, the electrodes being platinum wires, when persulphuric acid naturally appears at the positive pole.[64] When an acid of the strength $H_2SO_4,6H_2O$ is taken, at first only the hydrate of the sulphuric peroxide, S_2O_7,H_2O, is formed; but when the concentration about the positive pole reaches $H_2SO_4,3H_2O$, a mixture of hydrogen peroxide and the hydrate of sulphuric peroxide begins to be formed. Dilute solutions of sulphuric peroxide can be kept better than more concentrated solutions, but the latter may be obtained containing as much as 123 grams of the peroxide to a litre. It is a very instructive fact that

---

[63] Anhydrous **sulphuric peroxide**, S_2O_7, is obtained by the prolonged (8 to 10 hours) action of a silent discharge of considerable intensity on a mixture of oxygen and sulphurous anhydride; the vapour of sulphuric peroxide, S_2O_7, condenses as liquid drops or, after being cooled to 0°, in the form of long prismatic crystals, resembling those of sulphuric anhydride. The anhydrous compound, S_2O_7 (and also the hydrated compound), cannot be preserved long, as it splits up into oxygen and sulphuric anhydride. Direct experiment shows that a mixture of equal volumes of sulphurous anhydride and oxygen leaves a residue of ¾ of the oxygen taken, which indicates the formula S_2O_7. This substance is soluble in water, and it then gives a hydrate, probably having the composition $S_2O_7,H_2O=2SHO_4$.

In order to fully demonstrate the reality of a peroxide form for acids, it should be mentioned that some years ago Brodie obtained the so-called **acetic peroxide,** $(C_2H_3O)_3O_2$, by the action of barium peroxide on acetic anhydride, $(C_2H_3O)_2O$. Its corresponding hydrate is also known. A similar higher oxide has long been known for chromium.

[64] When an acid of the strength $H_2SO_4,6H_2O$ is taken, at first only the hydrate of the sulphuric peroxide, S_2O_7,H_2O, is formed, but when the concentration at the positive pole reaches $H_2SO_4,3H_2O$, a mixture of hydrogen peroxide and the hydrate of sulphuric peroxide begins to be formed. A state of equilibrium is ultimately arrived at when the amounts of these substances correspond with the proportion $S_2O_7 : 2H_2O_2$, which, as it were, answers to a new compound. But its existence cannot be admitted because the sulphuric peroxide can be easily distinguished from the hydrogen peroxide in the solution owing to the fact that the former does not act on an acid solution of potassium permanganate, whilst the hydrogen peroxide disengages both its own oxygen and that of the permanganic acid, which it converts into manganous oxide. Their common property of liberating iodine from an acid solution of the potassium iodide enables the sum of the active oxygen in them both to be determined. Elbs (1895) found by experiment that most $H_2S_2O_8$ is formed in electrolysis when the sulphuric acid taken has a sp. gr. from 1·35 to 1·5, i.e., with hydrates containing from $+7H_2O$ to $+3H_2O$.

hydrogen peroxide is always formed when strong solutions of persulphuric acid break up on keeping. So that the bond between the two peroxides is established both by analysis and synthesis: hydrogen peroxide is able to produce $S_2H_2O_8$, and the latter to produce hydrogen peroxide. A mixture of sulphuric peroxide with sulphuric acid or water is decomposed, with the evolution of oxygen, either when heated or under the action of spongy platinum. The same thing takes place with a solution of baryta, although at first no precipitate is formed and the decomposition of the barium salt, BaS_2O_8, with the formation of $BaSO_4$, only proceeds slowly, so that the solution may be filtered (the barium salt of persulphuric acid is soluble in water). Mercury, ferrous oxide, and the stannous salts are oxidised by $S_2H_2O_8$. These are all distinct signs of true peroxides. The same common properties (capacity for oxidising, property of forming peroxide of hydrogen, &c.) are possessed by the alkali salts of persulphuric acid, which are obtained by the action of an electric current upon certain sulphates, for instance, ammonium or potassium sulphate. The ammonium salt of persulphuric acid, $(NH_4)_2S_2O_8$, is especially easily formed by this means, and is now prepared on a large scale and used (like Na_2O_2 and H_2O_2) for bleaching tissues and fibres.[65]

---

[65] Marshall (1891) studied the formation of this class of compounds more fully; he subjected a saturated solution of bisulphate of potassium to electrolysis with a current of 3–3½ ampères; before electrolysis, dilute sulphuric acid is added to the liquid surrounding the negative pole, and during electrolysis the solution at the anode is cooled. The electrolysis is continued without interruption for two days, and a crystalline deposit separates at the anode. To avoid decomposition the latter is not filtered through paper, but through a perforated platinum plate, and dried on a porous tile. The mother liquor, with the addition of a fresh solution of bisulphate of potassium, is again subjected to electrolysis, and the crystals formed at the anode are again collected, &c. The salt so obtained may be recrystallised by dissolving it in hot water and rapidly cooling the solution after filtration; a small proportion of the salt is decomposed by this treatment. The composition of the salt is determined either by igniting it, when it forms sulphate of potassium, or else by titrating the active oxygen with permanganate; its composition was found to correspond with the salt of persulphuric acid, $K_2S_2O_8$. The solution of the salt has a neutral reaction, and does not give a precipitate with salts of other metals. $K_2S_2O_8$ is the most insoluble of the salts of persulphuric acid. With nitrate of silver it forms a salt, which gives peroxide of silver under the action of water, according to the equation: $Ag_2S_2O_8 + 2H_2O = Ag_2O_2 + 2H_2SO_4$. With an alkaline solution of a cupric salt (Fehling's solution) it forms a red precipitate of peroxide of copper. Manganese and cobalt salts give precipitates of MnO_2 and Co_2O_3. Ferrous salts are rapidly oxidised, while potassium iodide slowly disengages iodine at the ordinary temperature. All these reactions indicate the powerful oxidising properties of $K_2S_2O_8$. In oxidising in the presence of water it gives a residue of $KHSO_4$. The decomposition of the dry salt begins at 100°, but is not complete even at 250°. The freshly prepared salt is inodorous, but after being kept in a closed vessel it evolves a peculiar smell different from that of ozone. The ammonium salt, $(NH_4)_2S_2O_8$, is obtained in a similar manner. It is soluble to the extent of 58 parts per 100 parts by weight of water. The decomposition of the ammonium salt by the hydrated oxide of barium gives the barium salt, $BaS_2O_8,4H_2O$,

In order to understand the relation of sulphuric peroxide to sulphuric acid we must first remark that hydrogen peroxide is to be considered, in accordance with the law of substitution, as water, H(OH), in which H is replaced by (OH). Now the relation of $H_2S_2O_8$ to H_2SO_4 is exactly similar. The radicle of sulphuric acid, equivalent to hydrogen, is HSO_4;[65a] it corresponds with the (OH) of water, and therefore sulphuric acid, $H(SHO_4)$, gives $(SHO_4)_2$ or $S_2H_2O_8$, in exactly the same manner as water gives $(HO)_2$—i.e., H_2O_2.[66]

---

which is soluble to the extent of 52·2 parts in 100 parts of water at 0°. The crystals do not deliquesce in the air, and decompose in the course of several days. Solutions of the pure salt decompose slowly at the ordinary temperature. To completely decompose this salt it is necessary to boil its solution for a long time. Alcohol dissolves the solid salt; the anhydrous salt does not separate from the alcoholic solution, but a hydrate containing one molecule of water, BaS_2O_8,H_2O, which is soluble in water but insoluble in absolute alcohol. Sodium barium persulphate decomposes even when slightly heated. The free acid, which may serve for the preparation of other salts, is obtained by treating the barium salt with sulphuric acid. The lead salt, PbS_2O_8, has been obtained from the free acid; it crystallises with two or three molecules of water. It is soluble in water, deliquesces in the air, and with alkalies gives a precipitate of the hydrated oxide which rapidly oxidises into the binoxide.

Traube, before Marshall's researches, thought that the electrolysis of solutions of sulphuric acid did not give a hydrate of S_2O_7, but an oxide having the composition SO_4. On repeating his former researches (1892) Traube considers it very likely that the salts obtained by Marshall corresponded to an acid $H_2SO_4 + SO_4$, i.e., that the indifferent oxide, SO_4, can combine with sulphuric acid and form peculiar saline compounds. Traube, however, subsequently much doubted the truth of such a conclusion, but it afterwards lay at the basis of Baeyer and Villiger's conclusion (1901) regarding the independent existence of a special acid, $H_2SO_5 = H_2O + SO_4$. Lowry and West investigated the same subject somewhat earlier (1900), and came to the conclusion that peroxide of hydrogen gives three degrees of combination—$H_2O_2 + 1$ or 2 or $4SO_3$. The first is the H_2SO_5 just mentioned, the second is $H_2S_2O_8$, which is generally recognised, and the third, $H_2S_4O_{14}$, is stated by these authors to be formed in electrolysis. This question cannot yet be considered as decided. The acid having the composition $H_2SO_5 = H_2O_2,SO_3$ is known as 'Caro's reagent or acid,' and was obtained by mixing $H_2S_2O_8$ with dilute sulphuric acid; the resultant acid is highly oxidising, and converts aniline into nitrobenzene, &c. If it be supposed that $H_2S_2O_8$ combines with H_2O_2, formed from the same persulphuric acid, then the formation of H_2SO_5 may be understood, because $2H_2SO_5 = H_2S_2O_8 + H_2O_2$. This question requires further study.

[65a] Or one of those supposed ions which appear at the positive pole in the decomposition of sulphuric acid by the action of a galvanic current.

[66] If this be true, one would expect the following peroxide hydrates: for phosphoric acid, $(H_2PO_4)_2 = H_4P_2O_8 = 2H_2O + 2PO_3$; for carbonic acid, $(HCO_3)_2 = H_2C_2O_6 = H_2O + C_2O_5$; and for lead the true peroxide will be also Pb_2O_5, &c. Judging from the example of barium peroxide (note 62), these peroxide forms will probably combine together. It seems to me that the compounds obtained by Fairley for uranium are very instructive as elucidating the peroxides. In the action of hydrogen peroxide in an acid solution on uranium oxide, UO_3, there is formed a uranium peroxide, $UO_4,4H_2O, U = 240$), but hydrogen peroxide acts on uranium oxide in the presence of caustic soda; on the addition of alcohol a crystalline compound of the composition $Na_4UO_8,4H_2O$ is precipitated, which is doubtless a compound of the peroxides of sodium, Na_2O_2, and uranium, UO_4. It is very possible that the first peroxide, $UO_4,4H_2O$, contains the elements of hydrogen peroxide and uranium peroxide, U_2O_7, or even $U(OH)_6,H_2O_2$, just as the

The largest part **of the sulphuric acid made** is used for reacting, on sodium chloride in the manufacture of sodium carbonate; for the manufacture of the volatile acids, like nitric, hydrochloric, &c., from their corresponding salts; for the preparation of ammonium sulphate, alums, vitriols (copper and iron), artificial manures, superphosphate (Chap. XIX., note 18) and other salts of sulphuric acid; in the treatment of bone ash for the preparation of phosphorus, and for the solution of metals—for example, of silver in its separation from gold—for cleaning metals from rust, &c. A large amount of oil of vitriol is also used in the treatment of organic substances; it is used for the extraction of stearin, or stearic acid, from tallow, for refining petroleum and various vegetable oils, in the preparation of nitro-glycerine (Chap. VI., notes 37 and 37a), for dissolving indigo and other colouring matters, for the conversion of paper into vegetable parchment, for the preparation of ether from alcohol, for the preparation of various artificial scents from fusel oil, for the preparation of vegetable acids, such as oxalic, tartaric, and citric, for the conversion of non-fermentable starchy substances into fermentable glucose, and in a number of other processes. It would be difficult to find another artificially prepared substance which is so frequently applied in the arts as sulphuric acid. Where there are not works for its manufacture, the economical production of many other substances of great technical importance is impossible. In those localities which have arrived at a high technical activity the amount of sulphuric acid consumed is proportionately large; sulphuric acid, sodium carbonate, and lime are the most important of the artificially prepared agents employed in factories.

Besides the normal acids of sulphur, H_2SO_3, H_2SO_3S, and H_2SO_4, corresponding with sulphuretted hydrogen, H_2S, in the same way that $HClO_3$ and $HClO_4$ correspond with hydrochloric acid, HCl, there exists a peculiar series of acids which are termed **thionic acids.** Their general composition is $S_nH_2O_6$, where n varies from 2 to 5 and 6. If $n=2$, the acid is called dithionic acid. The others are distinguished as trithionic, tetrathionic, pentathionic, and hexathionic acids. Their composition, existence, and reactions are easily understood if they are referred to the class of the sulphonic acids—that is, if their relation to sulphuric acid is expressed in just the same manner as the relation of the organic acids to carbonic acid. The organic acids (Chap. IX.) proceed from the hydrocarbons by the substitution of

peroxide form lately discovered by Spring for tin perhaps contains Sn_2O_5,H_2O_2. Melikoff and Pisarjeffsky (1898) confirmed the composition UO_4. The chemistry of the peroxides is being investigated by many chemists, and L. Pisarjeffsky collected all the most important data on this most interesting subject in his work, *The Peroxides and Per-Acids* (Odessa, 1902).

their hydrogen by carboxyl—that is, by the radicle of carbonic acid, CHO_2. The formation of the acids of sulphur by means of sulphoxyl may be represented in the same manner, $HSO_3 = H_2SO_4 - HO$. Therefore to hydrogen, H_2, there should correspond the acids $H \cdot SHO_3$, sulphurous, and $SHO_3 \cdot SHO_3 = S_2H_2O_6$, or dithionic; to SH_2 there should correspond the acids $SH(SHO_3) = H_2S_2O_3$ (thiosulphuric), and $S(SHO_3)_2 = H_2S_3O_6$ (trithionic); to S_2H_2 the acids $S_2H(SHO_3) = H_2S_3O_2$ (unknown), and $S_2(SHO_3)_2 = H_2S_4O_6$ (tetrathionic); to $S_3H_2, S_3(SHO_3)_2 = H_2S_5O_6$ (pentathionic), and to H_2S_4, hexathionic acid, $(HSO_3)_2S_4 = H_2S_6O_6$.[66a] We know that iodine reacts directly with the hydrogen of sulphuretted hydrogen and combines with it, and if thiosulphuric acid contains the radicle of sulphuretted hydrogen (or hydrogen united with sulphur) of the same nature as in sulphuretted hydrogen, it is not surprising that iodine reacts with sodium thiosulphate and forms sodium tetrathionate. Thus, thiosulphuric acid, $HS(SHO_3)$, when deprived of H, gives a radicle which immediately combines with another similar radicle, forming the tetrathionate, $S_2(SO_2HO)_2$. According to this view[67] of the structure of the thionic acids and salts, it is also clear how all the thionic acids, like thiosulphuric acid, easily give sulphur and sulphides, with the exception only of dithionic acid, $H_2S_2O_6$, which, judging from the above, stands apart from the series of the other thionic acids. Dithionic acid stands in the same relation to sulphuric acid as oxalic acid does to carbonic. Oxalic acid is dicarboxyl, $(CHO_2)_2 = C_2H_2O_4$, and so also dithionic acid is disulphoxyl, $(SHO_3)_2 = S_2H_2O_6$. Oxalic acid, when ignited, decomposes into carbonic anhydride and carbonic oxide, CO, and dithionic acid, when heated, decomposes into sulphuric anhydride and sulphurous anhydride, SO_2, and SO_2 stands in the same relation to SO_3 as CO to CO_2. This also explains the peculiarity of the calcium, barium, and lead, &c. salts of the thionic acids being easily soluble (although the corresponding salts of H_2SO_3, H_2SO_4, and H_2S dissolve with difficulty), because the former are similar to the salts of the sulphonic acids, which are also soluble in water. Thus the thionic acids are **disulphonic acids,** just as many dicarboxylic acids are known—for example, $CH_2(CO_2H)_2$, $C_6H_4(CO_2H)_2$.[68]

[66a] A heptathionic acid, $(HSO_3)_3S_5$, should correspond to H_2S_5, but it has not yet been isolated.

[67] This view was communicated by me in 1870 to the Russian Chemical Society.

[68] **Dithionic acid,** $H_2S_2O_6$, is distinguished among the thionic acids as containing the least proportion of sulphur. It is also called hyposulphuric acid, because its supposed anhydride, S_2O_5, contains more O than sulphurous oxide, SO_2 or S_2O_4, and less than sulphuric anhydride, SO_3 or S_2O_6. Dithionic acid, discovered by Gay-Lussac and Welter, is known as a hydrate and in the form of salts, but not as anhydride. The method for preparing dithionic acid usually employed is by the action of finely powdered

Sulphur evidently exhibits an acid character, not only in its compounds with hydrogen and oxygen, but also in those with other elements.

manganese dioxide on a solution of sulphurous anhydride. On shaking, the smell of the latter disappears, and the manganese salt of the acid in question passes into solution; $MnO_2 + 2SO_2 = MnS_2O_6$. If the temperature is raised, the dithionate splits up into sulphurous anhydride and manganese sulphate, $MnSO_4$. Owing to this, a mixture of manganese sulphate and dithionate is generally obtained in the solution. These may be separated by mixing the solution of the manganese salts with a solution of barium hydroxide, when a precipitate of manganese hydroxide and barium sulphate is obtained. In this manner barium dithionate only is obtained in solution. It is purified by crystallisation, and separates as $BaS_2O_6,2H_2O$; this is then dissolved in water, and decomposed with the requisite amount of sulphuric acid. Dithionic acid, $H_2S_2O_6$, then remains in solution. By concentrating the resultant solution under the receiver of an air-pump it is possible to obtain a liquid of sp. gr. 1·847, but it still contains water, and on further evaporation the acid decomposes into sulphuric acid and sulphurous anhydride: $H_2S_2O_6 = H_2SO_4 + SO_2$. The same decomposition takes place if the solution is slightly heated. Like all the thionic acids, dithionic acid is readily attacked by oxidising agents, and passes into sulphurous acid. No dithionate is able to withstand the action of heat, even though very slight, without giving off sulphurous anhydride: $K_2S_2O_6 = K_2SO_4 + SO_2$. The alkali dithionates have a neutral reaction (which indicates the energetic nature of the acid), are soluble in water, and in this respect present a certain resemblance to the salts of nitric acid (their anhydrides are: N_2O_5 and S_2O_5). Klüss (1888) described many of the salts of dithionic acid.

Langlois, about 1840, obtained a peculiar thionic acid by heating a strong solution of acid potassium sulphite with flowers of sulphur to about 60°, until the disappearance of the yellow coloration first produced by the solution of the sulphur. On cooling, a portion of the sulphur was precipitated, and crystals of a salt of **trithionic acid,** $K_2S_3O_6$ (partly mixed with potassium sulphate), separated out. Plessy afterwards showed that the action of sulphurous acid on a thiosulphate also gives sulphur and trithionic acid: $2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S$. A mixture of potassium acid sulphite and thiosulphate also gives a trithionate. It is very possible that a reaction of the same kind occurs in the formation of trithionic acid by Langlois' method, because potassium sulphite and sulphur yield potassium thiosulphate. The potassium thiosulphate may also be replaced by potassium sulphide, and on passing sulphurous anhydride through the solution, thiosulphate is first formed and then trithionate: $4KHSO_3 + K_2S + 4SO_2 = 3K_2S_3O_6 + 2H_2O$. The sodium salt is not formed under the same circumstances as the corresponding potassium salt. The sodium salt does not crystallise and is very unstable: the barium salt is, however, more stable. The barium and potassium salts are anhydrous: they give neutral solutions and decompose when ignited, with the evolution of sulphur and sulphurous anhydride, a sulphate being left behind, $K_2S_3O_6 = K_2SO_4 + SO_2 + S$. If a solution of the potassium salt is decomposed by means of hydrofluosilicic or chloric acid, the insoluble salt of the acid used is precipitated and trithionic acid obtained in solution; this acid, however, very easily breaks up on concentration. The addition of salts of copper, mercury, silver, &c., to a solution of a trithionate is followed, either immediately or after a certain time, by the formation of a black precipitate of the sulphides whose formation is due to the decomposition of the trithionic acid with the transference of its sulphur to the metal.

Tetrathionic acid, $H_2S_4O_6$, in contradistinction to the preceding acids, is much more stable in the free state than in the form of salts. In the latter form it is easily converted into trithionate, with liberation of sulphur. Sodium tetrathionate was obtained by Fordos and Gélis by the action of iodine on a solution of sodium thiosulphate. The reaction consists essentially in the iodine taking up half the sodium of the thiosulphate. If in the above reaction the sodium thiosulphate be replaced by the lead salt, PbS_2O_3, the sparingly soluble lead iodide, PbI_2, and the soluble salt, PbS_4O_6, will be obtained. Moreover the lead salt easily gives tetrathionic acid itself ($PbSO_4$ is

The compound of sulphur and carbon has been particularly well investigated. It presents a great analogy to carbonic anhydride, in both its

precipitated). The solution of tetrathionic acid may be evaporated over a water-bath, and afterwards in a vacuum, when it gives a colourless liquid, which has no smell and a very acid reaction. When dilute it may be heated to its boiling-point, but in a concentrated form it decomposes into sulphuric acid, sulphurous anhydride, and sulphur: $H_2S_4O_6 = H_2SO_4 + SO_2 + S_2$.

Pentathionic acid, $H_2S_5O_6$, and **hexathionic acid**, $H_2S_6O_6$, also belong to this series of acids. But little is known concerning them, either as hydrates or in the form of salts. They are formed, together with other thionic acids, by the direct action of sulphurous acid on sulphuretted hydrogen (in excess) in aqueous solution, a large proportion of sulphur being precipitated at the same time; for instance, $5SO_2 + 5H_2S = H_2S_5O_6 + 5S + 4H_2O$.

If, as was shown above, the thionic acids are disulphonic acids, they may be obtained, like other sulphonic acids, by means of potassium sulphite and sulphur chloride. Thus, Spring demonstrated the formation of potassium trithionate by the action of sulphur dichloride on a strong solution of potassium sulphite, $2KSO_3K + SCl_2 = S(SO_3K)_2 + 2KCl$. If sulphur chloride is taken, sulphur is also precipitated. The same trithionate is formed by heating a solution of a double thiosulphate, for example, $AgKS_2O_3$. Two molecules of the salt then form silver sulphide and potassium trithionate. If the thiosulphate be the potassium silver salt, $SO_3K(AgS)$, then the structure of the trithionate must necessarily be $(SO_3K)_2S$. Previous to Spring's researches, the action of iodine on sodium thiosulphate was an isolated accidentally discovered reaction; he, however, showed its general significance by testing the action of iodine on mixtures of different sulphur compounds. Thus with iodine, I_2, the mixture $Na_2S + Na_2SO_3$ forms $2NaI + Na_2S_2O_3$, whilst the mixture $Na_2S_2O_3 + Na_2SO_3 + I_2$ gives $2NaI + Na_2S_3O_6$—that is, trithionic acid stands in the same relation to thiosulphuric acid as the latter does to sulphuretted hydrogen. And this is the above mode of representation: by replacing one hydrogen in H_2S by sulphoxyl we obtain thiosulphuric acid, $HSO_3{\cdot}HS$, and by replacing a second hydrogen in the latter again by sulphoxyl we obtain trithionic acid, $(HSO_3)_2S$. Furthermore, Spring showed that the action of sodium amalgam on the thionic acids causes reverse reactions to those above indicated for iodine. Thus, sodium thiosulphate with Na_2 gives $Na_2S + Na_2SO_3$, and Spring showed that the sodium here is not a simple element taking up sulphur, but itself enters into double decomposition, replacing sulphur; for on taking a potassium salt and acting on it with sodium, $KSO_3(SK) + NaNa = KSO_3Na + (SK)Na$. In a similar way sodium dithionate with sodium gives sodium sulphite: $(NaSO_3)_2 + Na_2 = 2NaSO_3Na$; sodium trithionate forms $NaSO_3Na$ and $NaSO_3{\cdot}SNa$, and the tetrathionate forms sodium thiosulphate, $(NaSO_3)S_2(NaSO_3) + Na_2 = 2(NaSO_3)(NaS)$.

In all the oxidised compounds of sulphur we may note the presence of the elements of sulphurous anhydride, SO_2, the only product of the combustion of sulphur, and in this sense the compounds of sulphur containing one SO_2 are—

$$SO_2{}^{H}_{HO} \qquad SO_2{}^{HO}_{HO} \qquad SO_2{}^{HS}_{HO} \qquad SO_2{}^{C_6H_5}_{HO}$$

Sulphurous acid	Sulphuric acid	Thiosulphuric acid	Benzene sulphonic acid

while, according to this mode of representation, the thionic acids are—

$$\begin{array}{c} HO \\ SO_2 \\ SO_2 \\ HO \end{array} \qquad \begin{array}{c} HO \\ SO_2 \\ \\ SO_2 \\ HO \end{array}\!\! S \qquad \begin{array}{c} HO \\ SO_2 \\ \\ SO_2 \\ HO \end{array}\!\! S_2 \qquad \begin{array}{c} HO \\ SO_2 \\ \\ SO_2 \\ HO \end{array}\!\! S_3$$

Dithionic	Trithionic	Tetrathionic	Pentathionic

Hence, it is evident that SO_2 has (whilst CO_2 has not) the faculty for combination, and aims at forming SO_2X_2, and in general SX_6. To this type, for instance, belong elementary composition and its chemical character. This substance is the so-called **carbon bisulphide**, CS_2, and corresponds with CO_2.

The first endeavours to obtain a compound of sulphur with carbon were unsuccessful, for although sulphur does combine directly with carbon, yet the formation of this compound requires distinctly definite conditions. If sulphur is mixed with charcoal and heated, it is simply driven off from the latter, and not the smallest trace of carbon bisulphide is obtained. The formation of this compound requires that the charcoal should be first heated to a red heat, but not above, and then either the vapour of sulphur passed over it or lumps of sulphur thrown on to the red-hot charcoal, but in small quantities, so as not to lower the temperature of the latter. If the charcoal is heated to a white heat, the amount of carbon bisulphide formed will be less. This depends, in the first place, on the dissociation of the carbon bisulphide at a high temperature.[69] In the second place, Favre and Silbermann showed that in the combustion of one gram of carbon bisulphide (the products will be $CO_2 + 2SO_2$) 3,400 heat units are evolved—that is, the combustion of a molecular quantity of carbon bisulphide evolves 258,400 heat units (according to Berthelot, 246,000). From a molecule of carbon bisulphide in grams we may obtain 12 grams of carbon, whose combustion evolves 96,000 heat units, and 64 grams of sulphur, evolving by combustion (into SO_2) 140,800 heat units. Hence we see that the component elements separately evolve less heat by their combustion (237,000 heat units) than carbon bisulphide itself—that is,

---

SO_3, SO_2Cl_2, $SO_2Cl(OH)$, and SF_6 (obtained by Moissan by the action of fluorine on sulphur), but neither SH_6 nor SCl_6 is known. In addition to what has been already said respecting the complex acids formed by sulphur, I think it well to mention that, according to the above view, still more complex oxygen acids and salts of sulphur may be looked for. For instance, the salt $Na_2S_4O_8$ obtained by Villiers (1888) is of this kind. It is formed together with sodium trithionate and sulphur, when SO_2 is passed through a cold solution of $Na_2S_2O_3$, which is then allowed to stand for several days at the ordinary temperature: $2Na_2S_2O_3 + 4SO_2 = Na_2S_4O_8 + Na_2S_3O_6 + S$. It may be assumed here, as in the thionic acids, that there are two sulphoxyls, bound together not only by S, but also by SO_2, or, what is almost the same thing, that the sulphoxyl is combined with the residue of trithionic acid, i.e., replaces one aqueous residue in trithionic acid.

[69] Even light decomposes carbon bisulphide, but not to the extent of separating carbon; under the action of the sun's rays it is decomposed into sulphur and a solid substance which is considered to be carbon monosulphide; it is of a red colour, and its sp. gr. is 1·66. (The formation of a red liquid compound, C_3S_2, has also been remarked.) Thorpe (1889) observed a complete decomposition of carbon bisulphide under the action of a liquid alloy of potassium and sodium; it is accompanied by an explosion and the deposition of carbon and sulphur. A similar complete decomposition of carbon bisulphide is also accomplished by the action of mercury fulminate (Chap. XVI., note 26), and is due to the fact that *at the ordinary temperature* (at which carbon bisulphide is not produced) *the decomposition* of carbon bisulphide takes place with the development of heat—that is, it represents an exothermal reaction, like the decomposition of all explosives.

that heat should be evolved (at the ordinary temperature) and not absorbed in its decomposition, and therefore that the formation of carbon bisulphide from charcoal and sulphur is in all probability accompanied by an absorption of heat.[70] It is therefore not surprising that, like other compounds produced with an absorption of heat (ozone, nitrous oxide, hydrogen peroxide, &c.), carbon bisulphide is unstable and easily converted into the original substances from which it is obtained. And indeed if the vapour of carbon bisulphide is passed through a red-hot tube, it is decomposed—that is, it dissociates—into sulphur and carbon. And this takes place at the temperature at which this substance is formed, just as water decomposes into hydrogen and oxygen at the temperature of its formation. By this absorption of heat in the formation of carbon bisulphide is explained the facility with which it suffers reactions of decomposition, which we shall see in the sequel, and its main difference from the closely analogous carbonic anhydride.

In the laboratory carbon bisulphide is prepared as follows: A porcelain tube is luted into a furnace in an inclined position, the upper extremity of the tube being closed by a cork, and the lower end connected with a condenser. The tube contains charcoal, which is raised to a red heat, and pieces of sulphur are then placed in the upper end. The sulphur melts, and its vapour comes into contact with the red-hot charcoal, when combination takes place; the vapours condense in a well-cooled condenser, carbon bisulphide being a liquid boiling at 48°. On a large scale the apparatus depicted in fig. 101 is employed. A cast-iron cylinder rests on a stand in a furnace. Wood charcoal is charged into the cylinder through the upper tube closed by a clay stopper, while the sulphur is introduced through a tube reaching to the bottom of the cylinder. Pieces of sulphur thrown into this tube

---

[70] The fact should not be lost sight of that sulphur and charcoal are solids at the ordinary temperature, whilst carbon bisulphide is a very volatile liquid, and consequently, in the act of combination, referred to the ordinary temperature, there is, as it were, a passage into a liquid state, and this requires the absorption of heat. And, furthermore, the molecule of sulphur contains at least six atoms, and the molecule of carbon in all probability (Chap. VIII.) a very considerable number of atoms; thus, the action of sulphur on charcoal may be expressed in the following manner: $3C_n + nS_6 = 3nCS_2$; that is, from $n + 3$ molecules there proceed $3n$ molecules, and as n must be very considerable, $3n$ must be greater than $3 + n$, which indicates a decomposition in the formation of carbon bisulphide, although the reaction at first sight appears as one of combination. This decomposition is seen also from the volumes in the solid and liquid states. Carbon bisulphide has a sp. gr. of 1·29; hence its molecular volume is 59. But the volume of carbon, even in the form of charcoal, is not more than 6, and the volume of S_2 is 30; hence 36 volumes after combination give 59 volumes—an expansion takes place, as in decompositions. The physical work of converting the solids (sulphur and carbon) into a liquid, the mechanical work of increasing the volume, and the chemical work of depolymerisation of the carbon and sulphur naturally require much heat. This example illustrates the complexity of thermo-chemical phenomena.

fall on to the bottom of the cylinder, and are converted into vapour, which passes through the entire layer of charcoal in the cylinder. The vapour of carbon bisulphide thus formed passes through the exit tube, first into a Woulfe's bottle (where the sulphur which has not entered into the reaction is condensed), and then into a strongly cooled condenser or worm.[71]

Pure carbon bisulphide is a colourless liquid, which refracts light strongly, and has a pure ethereal smell; at 0° its specific gravity is 1·293, and at 15°, 1·271. If kept for a long time it seems to undergo a change, especially when it is kept under water, in which it is insoluble. It boils at 48°, and the pressure of its vapour is so great that it evaporates very easily, producing cold,[72] and therefore it has to be kept in well-stoppered vessels; it is generally kept under a layer of water, which hinders its evaporation and does not dissolve it.[73]

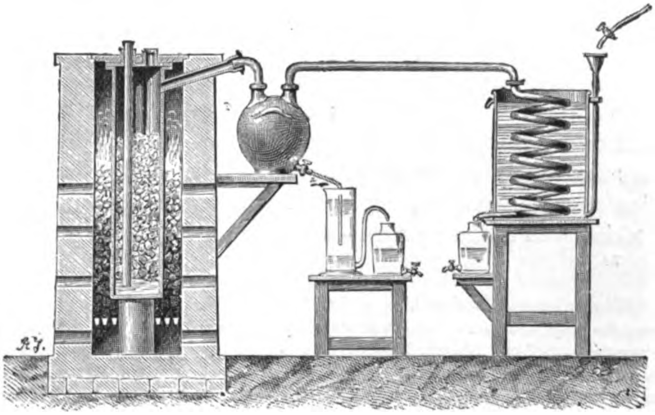


FIG. 101.—Apparatus for the manufacture of carbon bisulphide.

---

[71] Carbon bisulphide, as prepared on a large scale, is generally very impure, and contains not only sulphur, but, more especially, other impurities which give it a very disagreeable odour. The best method of purifying this malodorous carbon bisulphide is to shake it up with a certain amount of mercuric chloride, or even simply with mercury, until the surface of the metal ceases to turn black. After this the carbon bisulphide must be poured off and distilled over a water-bath, after mixing with some oil to retain the impurities.

[72] If carbon bisulphide be evaporated under the receiver of an air-pump, or by means of a current of air, it is possible to obtain a temperature as low as −60°, and the carbon bisulphide does not solidify at this temperature. However, if a series of air-bubbles is passed through it by means of bellows, a crystalline white substance remains which volatilises below 0°: this is a hydrate, $H_2O,2CS_2$, which easily decomposes into water and carbon bisulphide. It is formed in the above experiment by the moisture held in the air passed through the carbon bisulphide, and by the fall of temperature.

[73] Strong alcohol is miscible in all proportions with carbon bisulphide, but dilute alcohol only in a definite amount, owing to its diminished solubility from the presence of the water in it. Ether, hydrocarbons, fatty oils, and many other organic substances are

Carbon bisulphide enters into many combinations, which are frequently closely analogous to the compounds of carbonic anhydride. In this respect it is a **thio-anhydride**—i.e., it has the character of the acid anhydrides,[73a] like carbonic anhydride, with the difference that the oxygen of the latter is replaced by sulphur. By thio-compounds are understood, in general, those compounds of sulphur which correspond with the oxygen compounds, but with substitution of sulphur for oxygen. Thus, thiosulphuric acid is mono-thiosulphuric acid—that is, sulphuric acid in which one atom of sulphur replaces one atom of oxygen. With the sulphides of the alkalies and alkaline earths, it forms saline substances corresponding with the carbonates, and these compounds may be termed **thio-carbonates.** For example, the composition of the sodium salt, Na_2CS_3, is exactly like that of sodium carbonate. These salts are formed by the direct solution of carbon bisulphide in aqueous solutions of the sulphides ; but they are difficult to obtain in a crystalline form, because they are easily decomposable. When their solutions are highly concentrated they begin to decompose, with the evolution of sulphuretted hydrogen and the formation of a carbonate, water taking part in the reaction—for example, $K_2CS_3 + 3H_2O = K_2CO_3 + 3H_2S$.[74]

---

soluble with great ease in carbon bisulphide. This is taken advantage of in practice for extracting the fatty oils from vegetable seeds, such as linseed, palm-nuts, or from bones, &c. The preparation of vegetable oils is usually carried out by pressing the seeds under a press, but the residue always contains a certain amount of oil. These traces of oil can, however, be removed by treatment with carbon bisulphide. In this manner a solution is obtained which when heated readily parts with all the carbon bisulphide, leaving the non-volatile fatty oil behind, so that the same carbon bisulphide may be condensed and used over again for the same purpose. It also dissolves iodine, bromine, indiarubber, sulphur, and certain resins.

Carbon bisulphide, especially at high temperatures, very often acts by its elements in a manner in which carbon and sulphur alone are not able to react, which will be understood from what has been said above respecting its endothermal origin. If it is passed over red-hot metals—over copper, for instance, not to mention sodium, &c.—it forms a sulphide of the metal and deposits charcoal, and if the vapour is passed over incandescent metallic oxides it forms metallic sulphides and carbonic anhydride (and sometimes a certain amount of sulphurous anhydride). Lime and similar oxides give under these circumstances a carbonate and a sulphide—for example, $CS_2 + 3CaO = 2CaS + CaCO_3$. The sulphides obtained by this means are often well crystallised, like those found in nature—for example, lead and antimony sulphides.

[73a] And just as $COCl_2$ corresponds to CO_2, so also the chloranhydride, $CSCl_2$, or *thiophosgene*, corresponds to CS_2.

[74] If instead of a sulphide we take an alkali hydroxide, a thiocarbonate is also formed, together with a carbonate—thus, $3BaH_2O_2 + 3CS_2 = 2BaCS_3 + BaCO_3 + 3H_2O$. From the instability of the thiocarbonates of the alkaline metals we can clearly see the reason of the difficulty with which the salts of the heavier metals are formed, whose basic properties are incomparably weaker. However, these salts may be obtained by double decomposition. The potassium salt, K_2CS_3, is employed in vineyards as a preventive of phylloxera.

Carbon bisulphide forms compounds not only with the metallic sulphides, but also

A remarkable example [74a] of the thio-compounds is found in **thiocyanic acid**—i.e., cyanic acid in which the oxygen is replaced by sulphur, HCNS. We know (Chap. IX.) that with oxygen the cyanides of the alkaline metals, RCN, give cyanates, RCNO; but they also combine with sulphur, and therefore if yellow prussiate of potash be treated as in the preparation of potassium cyanide, and sulphur be added to the mass, **potassium thiocyanate**, KNCS, will be obtained in solution. This salt is much more stable than potassium cyanate; it dissolves without change in water and alcohol, forming colourless solutions from which it easily crystallises on evaporation; it may be kept exposed to air even when in solution. In dissolving in water it absorbs a considerable amount of heat, and forms the starting-point for the preparation of all the thiocyanates, RCNS, and organic compounds in which the metals are replaced by hydrocarbon groups. Such, for example, is volatile mustard oil, C_3H_5CSN (allyl thiocyanate),[75] which gives to mustard its caustic properties. With ferric salts the thiocyanates give an exceedingly brilliant red coloration, which serves for

---

with sulphuretted hydrogen—that is, it forms **thiocarbonic acid**, H_2CS_3. This is obtained by carefully mixing solutions of thiocarbonates with dilute hydrochloric acid, and separates in an oily layer, which easily decomposes in the presence of water into sulphuretted hydrogen and carbon bisulphide, just as the corresponding carbonic acid (hydrate) decomposes into water and carbonic anhydride. Carbon bisulphide combines not only with sodium sulphide, but also with the bisulphide, Na_2S_2, not, however, with the trisulphide, Na_2S_3. Organic compounds, like alcohol, C_2H_5OH or EtOH, when treated with caustic alkalies and CS_2 give xanthates, (EtO)(MS)CS, which are yellow and easily decompose. Cellulose, $C_6H_{10}O_5$, has the faculty of entering into a similar form of reaction, in the state of fibre or otherwise. When treated with a solution of NaHO it forms a sodium derivative (part of the H in OH is replaced by Na), and this, with CS_2, forms a xanthic compound which is reconverted into cellulose by the action of acids. This reconverted cellulose has the appearance of a viscid gelatinous mass known as **viscose**, which can be drawn into threads, formed into films, and used to attach (glue) objects together. After drying, there remains cellulose, for instance in the form of fibre, having a silky lustre, transparent and elastic, &c. This discovery of Cross and Bevan (1896) may find many most useful applications, and is already employed for the manufacture of artificial silk.

[74a] The relation of carbon bisulphide to the carbon compounds presents many other most interesting features which are considered in organic chemistry. We will here turn our attention to organic sulphides. Ethyl sulphide, $(C_2H_5)_2S$, combines with ethyl iodide, C_2H_5I, forming a molecule, $S(C_2H_5)_3I$. This compound is of a saline character, corresponds with salts of the alkalies, and is closely analogous to ammonium chloride. It is soluble in water; when heated, it again splits up into its components EtI and Et_2S, and with silver hydroxide gives a hydroxide, $Et_3S{\cdot}OH$, having the property of a distinct and energetic alkali, resembling caustic ammonia. Hence, sulphur here enters into a relation towards other elements similar to that of nitrogen in ammonia and ammonium salts. Judging from the existence of the ethyl-sulphine compounds, it might be imagined that sulphur forms a compound, SH_4, with hydrogen; but no such compound is known, just as NH_5 is unknown, although NH_4Cl exists.

[75] Although mustard oil may be obtained from the thiocyanates, it is only an isomeride of allyl thiocyanate proper, as is explained in organic chemistry.

detecting the smallest traces of ferric salts in solution. Thiocyanic acid, HCNS, may be obtained by a method of double decomposition, by distilling potassium thiocyanate with dilute sulphuric acid. It is a volatile colourless liquid, having a smell recalling that of vinegar, is soluble in water, and may be kept in solution without change.[75a] The thiocyanates are fully described in works on organic chemistry.

The sulphur compounds of chlorine, Cl_2S and Cl_2S_2, may be regarded as products, on the one hand, of the metalepsis of H_2S and H_2S_2, and, on the other hand, of the oxygen compounds of chlorine, because chloride of sulphur, Cl_2S, resembles chlorine oxide, Cl_2O ; or, thirdly, we may see in these compounds the type of the acid chloranhydrides, because they are all decomposed by water, forming hydrochloric acid, and sulphur tetrachloride, SCl_4, corresponds to SO_2 just as PCl_3 does to P_2O_3, and forms HCl and SO_2 with water.[76]

The **compounds of sulphur with chlorine** are prepared in the apparatus depicted in fig. 102. As sulphur chloride is decomposed by water, the chlorine evolved in the flask C must be dried before coming into contact with the sulphur. It is therefore passed first through a Woulfe's bottle, B, containing sulphuric acid, and then through the

---

[75a] Sulphur can only replace half the oxygen in CO_2, as is seen in **carbon oxysulphide**, or monothiocarbonic anhydride, COS. This substance was obtained by Than, and is formed in many reactions. A certain amount is obtained if a mixture of carbonic oxide and the vapour of sulphur is passed through a red-hot tube. When carbon tetrachloride is heated with sulphurous anhydride, this substance is also formed; but it is best obtained in a pure form by decomposing potassium thiocyanate with a mixture of equal volumes of water and sulphuric acid. A gas is then evolved containing a certain amount of hydrocyanic acid, from which it may be freed by passing it over wool containing moistened mercuric oxide, which retains the hydrocyanic acid. The reaction is expressed by the equation: $2KCNS + 2H_2SO_4 + 2H_2O = K_2SO_4 + (NH_4)_2SO_4 + 2COS$. It is also formed by passing the vapour of carbon bisulphide over alumina or clay heated to redness (Gautier; silicon sulphide is then formed). COS is also formed by passing phosgene over a long layer of asbestos mixed with sodium sulphide at 270°; $CdS + COCl_2 = CdCl_2 + COS$ (Nuricsán, 1892). The pure gas has an aromatic odour, is soluble in its own volume of water, which, however, acts on it, so that it must be collected over mercury. When slightly heated, carbon oxysulphide decomposes into sulphur and carbonic oxide. It burns in air with a pale blue flame, explodes with oxygen, and yields potassium sulphide and carbonate with potassium hydroxide: $COS + 4KHO = K_2CO_3 + K_2S + 2H_2O$.

[76] There is no reason for seeing any contradiction or mutual incompatibility in these three views, because every analogy is more or less modified by a change of elements. Thus, for instance, it cannot be expected that the product of the metalepsis of hydrogen sulphide would resemble the corresponding products of water in all respects, because water has not the acid properties of hydrogen sulphide. In the days of dualism and electrical polarity it was supposed that the sulphur varied in its nature: in hydrogen sulphide or potassium sulphide it was considered to be negative, and in sulphurous anhydride or sulphur dichloride, positive. This differs but little from the view held by those who consider that sulphur is divalent in some compounds (H_2S, SCl_2), tetravalent in others (SO_2, SCl_4, SEt_3T), and hexavalent in others (SO_3, SF_6), and that it is different in each of these states.

cylinder D containing pumice-stone moistened with sulphuric acid, and is then led into the retort E, in which the sulphur is heated. The compound which is formed distils over into the receiver R. A certain amount of sulphur passes over with the sulphur chloride, but if the resultant distillate is re-saturated with chlorine and distilled no free sulphur remains, the boiling-point rises to 144°, and pure **sulphur chloride**, S_2Cl_2, is obtained. Its formula is doubled because its vapour density referred to hydrogen is 68. It is also obtained by heating certain metallic chlorides (stannous, mercuric) with sulphur; both the metal and chlorine then combine with the sulphur. Sulphur chloride is a yellowish-brown liquid, which boils at 144°, and has a specific gravity of 1·70 at 0°. It fumes strongly in the air, reacting on the moisture contained therein, and has a heavy chloranhydrous odour. It dissolves sulphur, is miscible with carbon bisulphide, and falls to the bottom of a vessel containing water, by which it is decomposed, forming sulphurous anhydride and hydrochloric acid; but it first forms various lower stages of oxidation of sulphur, because the addition of silver nitrate to the solution gives a black precipitate. With hydrogen sulphide it gives sulphur and hydrochloric acid, and it reacts directly with metals—especially arsenic, antimony, and tin—forming sulphides and chlorides. In the cold, it absorbs chlorine and gives **sulphur dichloride**, SCl_2. The entire conversion into this substance requires the prolonged passage of dry chlorine through sulphur chloride surrounded by a freezing mixture. The distillation of the dichloride must be conducted in a stream of chlorine, as otherwise it partially

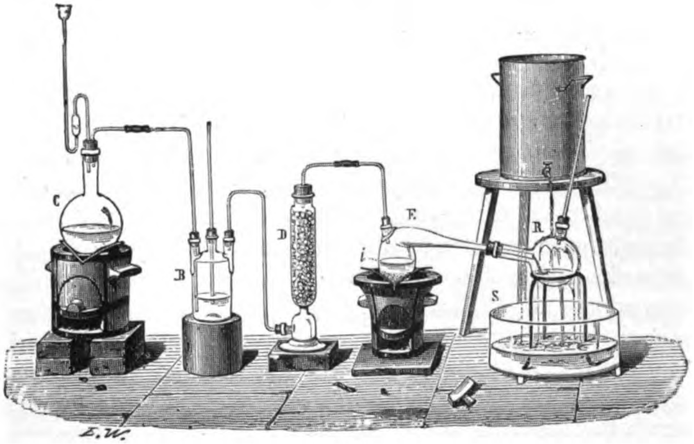


FIG. 102.—Apparatus for the preparation of sulphur chloride, and similar volatile compounds prepared by combustion in a stream of chlorine.

decomposes into sulphur chloride and chlorine. Pure sulphur dichloride is a reddish-brown liquid, which resembles the lower chloride in many respects; its specific gravity is 1·62; its odour is more suffocating than that of sulphur chloride; it volatilises at 64°.[77]

Thionyl chloride, $SOCl_2$, may be regarded as oxidised sulphur dichloride; it corresponds with sulphur chloride, S_2Cl_2, in which one atom of sulphur is replaced by oxygen. At the same time it is chlorine oxide (hypochlorous anhydride, Cl_2O) combined with sulphur, and also the chloranhydride of sulphurous acid—that is, $SO(HO)_2$, in which the two hydroxyl groups are replaced by two atoms of chlorine, or sulphurous anhydride, SO_2, in which one atom of oxygen is replaced by two atoms of chlorine. All these representations are confirmed by reactions of formation or decomposition; they all agree with our notions of the other compounds of sulphur, oxygen, and chlorine. Thionyl chloride was first obtained by Schiff by the action of dry sulphurous anhydride on phosphorus pentachloride. On distilling the resultant liquid, thionyl chloride comes over first at 80°, and on continuing the distillation phosphorus oxychloride distils over at above 100°, $PCl_5 + SO_2 = POCl_3 + SOCl_2$. This mode of preparation is direct evidence of the oxychloride character of $SOCl_2$. Würtz obtained the same substance by passing a stream of chlorine oxide through a cold solution of sulphur in sulphur chloride; the chlorine oxide then combined directly with the sulphur, $S + Cl_2O = SOCl_2$, whilst the sulphur chloride remained unchanged (sulphur explodes with chlorine oxide). Thionyl chloride is a colourless liquid, with a suffocating acrid smell; it has a specific gravity at 0° of 1·675, and boils at 78°. It sinks in water, by which it is immediately decomposed, like all chloranhydrides—for example, like

---

[77] The observed vapour density of sulphur dichloride referred to hydrogen is 53·3, and that given by the formula, 51·5. The smaller molecular weight explains its boiling-point being lower than that of sulphur chloride, S_2Cl_2. The reactions of these two compounds are very similar. Sulphur converts the dichloride, SCl_2, into the monochloride, S_2Cl_2. In one point the dichloride differs distinctly from the monochloride—that is, in its capacity for easily giving up chlorine and decomposing. Even light decomposes it into chlorine and the monochloride. Hence it acts on many substances in the same manner as chlorine, or substances which easily part with the latter, such as phosphoric or antimonic chloride. In distinction from these, however, sulphur dichloride would appear to distil without any considerable decomposition, judging by the vapour density. But this is not a valid conclusion, for if there be a decomposition, then $2SCl_2 = S_2Cl_2 + Cl_2$; now the density of sulphur chloride is 67·5, and that of chlorine, 35·5, and consequently a mixture of equal volumes of the two would give 51·5, just the same as sulphur dichloride. *Therefore the distillation of sulphur dichloride is probably nothing but its decomposition,* and it must then be admitted that the compound SCl_2, which is stable at the ordinary temperature, decomposes at 64°. On cooling to −25° it absorbs a further amount of chlorine, corresponding to SCl_4, but even at −10° a portion of the absorbed chlorine is given off—that is, dissociation takes place. Thus the tetrachloride is even less stable than the dichloride. SCl_2 and SCl_4 are able to combine with $SnCl_4$, $AsCl_3$, &c., forming solid crystalline substances.

carbonyl chloride, which corresponds with it: $SOCl_2+H_2O=SO_2+2HCl$.[77a]

Normal sulphuric acid has two corresponding chloranhydrides; the first, $SO_2(OH)Cl$, is sulphuric acid, $SO_2(HO)_2$ in which one equivalent of HO is replaced by chlorine; the second has the composition SO_2Cl_2—that is, two HO groups are substituted by two of chlorine. It is called **sulphuryl chloride**, and the first chloranhydride, SO_2HOCl, may be called chlorosulphonic acid, because it retains one hydroxyl of sulphuric acid, and its corresponding salts are known. Thus, potassium chloride absorbs the vapour of sulphuric anhydride, forming a salt, SO_3KCl, corresponding with SO_3HCl as acid. This first chloranhydride of sulphuric acid, SO_2HOCl, discovered by Williamson, is obtained either by the action of phosphorus pentachloride (or even $POCl_3$) on sulphuric acid ($PCl_5+H_2SO_4=POCl_3+HCl+HSO_3Cl$), or directly by the action of dry hydrochloric acid on sulphuric anhydride, $SO_3+HCl=HSO_3Cl$. The most easy and rapid method of its formation is by direct saturation of cold Nordhausen acid with dry hydrochloric acid gas ($SO_3+HCl=HSO_3Cl$), and distillation of the resultant solution; the distillate then contains HSO_3Cl. It is a colourless fuming liquid, having an acrid odour; it boils at 153° (according to my determination, confirmed by Konovaloff), and its specific gravity at 19° is 1·776. It is immediately decomposed by water, forming hydrochloric and sulphuric acids, as should be the case with a true chloranhydride. In the reactions of this chloranhydride we find the easiest means of introducing the sulphonic group HSO_3 into other compounds, because it is here combined with chlorine. **Sulphuryl chloride**, SO_2Cl_2, was obtained by Regnault by the direct action of the sun's ray (or in the presence of acetic acid or carbon, or, better still, in the presence of camphor) on a mixture of equal volumes of chlorine and sulphurous oxide. The gases gradually condense into a liquid, combining together as carbonic oxide does with chlorine. The first chloranhydride, SO_3HCl, decomposes, when heated at 200° in a closed tube, into sulphuric acid and sulphuryl chloride. It boils at 76°, its specific gravity is 1·70, it gives hydrochloric and sulphuric acids[77b] with water, fumes in the air,

---

[77a] Hartog and Sims (1893) obtained thionyl bromide, $SOBr_2$, by treating $SOCl_2$ with sodium bromide; it is a red liquid of sp. gr. 2·62, and decomposes at 150°. Thorpe and Rodger (1889), by heating a mixture of lead fluoride and phosphorus pentasulphide to 250° in an atmosphere of dry nitrogen, obtained gaseous **phosphorus fluosulphide** or thiophosphoryl fluoride, PSF_3, corresponding with $POCl_3$. This colourless gas is converted into a colourless liquid by a pressure of 11 atmospheres; it does not act upon dry mercury and takes fire spontaneously in air or oxygen, forming phosphorus pentafluoride, phosphorous anhydride, and sulphurous anhydride.

[77b] Baeyer and Villiger obtained a crystalline compound, SO_2Cl_2, with water in the cold. It is an interesting but little-known compound.

and, judging by its vapour density, does not decompose when distilled.[78]

Moissan and Lebeau (1900) obtained **hexafluoride of sulphur**, SF_6, by the direct action of free fluorine on sulphur (absorbing the foreign gases in KHO). It crystallises at −55°, has no smell or taste, and is only slightly soluble in water. Its density compared with that of hydrogen is 72 (according to its formula, 63·5). It is not acted on by alkalies, even with the aid of heat, and is almost as inactive as nitrogen. However, if this gas is mixed with hydrogen and a series of electric sparks passed through the mixture, it is decomposed with the formation of HF, H_2S, sulphur, &c. The formation of this remarkable substance clearly shows the power of sulphur to give, like the elements of group VI., compounds of the type SX_6, an instance of which is seen in sulphuric acid itself, $SO_2(OH)_2$.[78a]

[78] Pyrosulphuryl chloride, $S_2O_5Cl_2$. See note 44. Thorpe and Kirman, by treating SO_3 with HF, obtained $SO_2(OH)F$, as a liquid boiling at 163°, but which decomposed with great facility and then gave SO_2F_2.

[78a] The acids of sulphur naturally have their corresponding ammonium salts, and the latter their amides and nitriles. It will be readily understood how vast a field for research is presented by the series of compounds of sulphur and nitrogen, if we only remember that, as we saw in Chap. IX., there is a vast series of derivatives corresponding with the ammonium salts of carbonic and formic acids. To sulphuric acid there correspond: two ammonium salts, $SO_2(HO)(NH_4O)$ and $SO_2(NH_4O)_2$; three amides—the acid amide, $SO_2(HO)(NH_2)$, or sulphamic acid, the normal saline compound $SO_2(NH_4O)(NH_2)$, or ammonium sulphamate, and the normal amide $SO_2(NH_2)_2$, or sulphamide (the analogue of urea); then the acid nitrile, SON(HO), and two neutral nitriles, $SON(NH_2)$ and SN_2. There are similar compounds corresponding with sulphurous acid, and therefore its nitriles will be, an acid, SN(HO), its salt and the normal compound, $SN(NH_2)$. Dithionic and the other acids of sulphur should also have their corresponding amides and nitriles. Only a few examples are known, which we shall briefly describe. Sulphuric acid forms salts of very great stability with ammonia, and ammonium sulphate is one of the commonest ammoniacal compounds. It is obtained by the direct action of ammonia on sulphuric acid, or by the action of the latter on ammonium carbonate; it separates from its solutions in an anhydrous state, like potassium sulphate, with which it is isomorphous. Hence the composition of the crystals of **ammonium sulphate** is $(NH_4)_2SO_4$. This salt fuses at 140°, and does not undergo any change when heated up to 180°. At higher temperatures it does not lose water, but parts with half its ammonia, and is converted into the acid salt, HNH_4SO_4; and this acid salt, on further heating, undergoes a further decomposition, and splits up into nitrogen, water, and acid ammonium sulphite, HNH_4SO_3. At the ordinary temperature the normal salt is soluble in twice its weight of water and at the boiling-point of water in an equal weight. In its faculty for combination this salt exhibits a great resemblance to potassium sulphate, and, like it, easily forms a number of double salts, the most remarkable of which are the ammonia alums, $NH_4AlS_2O_8,12H_2O$, and the double salts formed by the metals of the magnesium group, having, for example, the composition $(NH_4)_2MgS_2O_8,6H_2O$. Ammonium sulphate does not give an amide when heated, perhaps owing to the power of sulphuric anhydride of retaining the water combined with it with great force. But the amides of sulphuric acid may be very conveniently prepared from sulphuric anhydride. Their formation by this method is very easily understood, because an amide is equal to an ammonium salt less water, and if the anhydride be taken it will give an amide directly with ammonia. Thus, if dry ammonia is passed into

In the group of the halogens we saw four closely analogous elements —fluorine, chlorine, bromine, and iodine—and we meet with the same

a vessel surrounded by a freezing mixture and containing sulphuric anhydride, it forms a white powdery mass called **sulphatammon**, having the composition $SO_3,2H_3N$ and resembling the similar compound of carbonic acid, $CO_2,2NH_3$. This substance is naturally the ammonium salt of sulphamic acid, $SO_2(NH_4O)NH_2$. It is slowly acted on by water, and may therefore be obtained in solution, in which it slowly reacts with barium chloride, which proves that with water it still forms ammonium sulphate. If this substance is carefully dissolved in water and evaporated, it yields well-formed crystals, whose solution no longer gives a precipitate with barium chloride. This is due to a change in the nature of the substance, and therefore Rose calls the crystalline modification **parasulphatammon**. Platinum chloride only precipitates half the nitrogen as platinochloride from solutions of sulphat- and parasulphat-ammon, which shows that they are ammonium salts, $SO_2(NH_4O)(NH_2)$. It may be that the reason of the difference in the two modifications is connected with the fact that two different substances of the composition $N_2H_4SO_2$ are possible: one is the amide $SO_2(NH_2)_2$, corresponding with the normal salt, and the other is the salt of the nitrile acid, corresponding with acid ammonium sulphate—that is, $SON(ONH_4)$ corresponds with the acid $SON(OH) = SO_2(NH_4O)OH - 2H_2O$. Hence, there may here be a difference of the same nature as that between urea and ammonium cyanate. Up to the present, the isomerism indicated above has been but little investigated, and might be the subject of interesting researches.

If in the preceding experiment the ammonia, and not the sulphuric anhydride, is taken in excess, a soluble subtance of the composition $2SO_2,3NH_3$ is formed. This compound, obtained by Jacqueline and investigated by Voronin, doubtless also contains a salt of sulphamic acid—that is, of the amide corresponding with the acid ammonium sulphate $= HNH_4SO_4 - H_2O = (NH_2)SO_2(OH)$. Probably it is a compound of sulphatammon with sulphamic acid. Thus it has an acid reaction, and does not give a precipitate with barium chloride.

With normal sulphate of ammonium, an amide of the composition $N_2H_4SO_2$ should correspond, which should bear the same relation to sulphuric acid as urea bears to carbonic acid. This amide, known as **sulphamide**, is obtained by the action of dry ammonia on the sulphuryl chloride, SO_2Cl_2: $SO_2Cl_2 + 4NH_3 = N_2H_4SO_2 + 2NH_4Cl$, just as urea is obtained by the action of ammonia on carbonyl chloride. The ammonium chloride is separated from the resultant sulphamide with great difficulty. Cold water, acting on the mixture, dissolves them both; the cold solution does not give a precipitate with barium chloride. Alkalies act on it slowly, as they do on urea; but on boiling, especially in the presence of alkalies or acids, it easily re-combines with water, and gives an ammonium salt. V. Traube (1892) obtained sulphamide by the reaction of sulphuryl chloride dissolved in chloroform upon ammonia. The resultant precipitate dissolves when shaken up with water, and the solution (after boiling with the oxides of lead or silver) is evaporated, when a syrupy liquid remains. With nitrate of silver the latter gives a solid compound, which, when decomposed by hydrochloric acid, gives free sulphamide in large colourless crystals, having the composition $SO_2(NH_2)_2$. This substance fuses at 81°, begins to decompose below 100°, and is entirely decomposed above 250°; it is soluble in water, and the solution has a neutral reaction and bitter taste. When heated with acids, sulphamide gradually decomposes, forming sulphuric acid and ammonia. If the silver compound obtained by the action of sulphamide on nitrate of silver is heated at 170°–180° until ammonia is no longer evolved, and the residue extracted with water acidulated with nitric acid, a salt separates out from the solution, answering in its composition to sulphamide, SO_2NAg, which = the amide $- NH_3 = SO_2N_2H_4 - NH_3 = SO_2NH$. The action of sulphuryl chloride (and of the other chloranhydrides of sulphur) on ammonium carbonate always, as Mente showed (1888), results in the formation of the salt $NH(SO_3NH_4)_2$.

The nitriles corresponding with sulphuric acid are not as yet known with any number of closely allied analogues in the oxygen group; for besides sulphur this group also includes **selenium** and **tellurium**: O, S, Se, Te. These two groups are very closely allied, both in respect to the magnitudes of their atomic weights and also in the faculty of the elements of both groups for combining with metals. The distinct analogy and definite degree of variance known to us for the halogens also repeat themselves in the same degree for the elements of the oxygen group. Amongst the halogens, fluorine has many peculiarities compared with Cl, Br, and I, which are more closely analogous, whilst oxygen differs in many respects from S, Se, Te, which possess greater similarities. The analogy in a quantitative respect is perfect in both cases. Thus the halogens combine with H, and the elements of the oxygen group with

---

certainty. The most simple nitrile corresponding with sulphuric acid should have the composition $N_2H_3SO_4 - 4H_2O = N_2S$. This would be a kind of cyanogen corresponding with sulphuric acid. On comparing sulphurous acid with carbonic acid we saw that they present a great analogy in many respects, and therefore it might be expected that nitrile compounds having the composition NHS and N_2S_2 would be found. The latter of these compounds is well known, and was obtained by Soubeiran by the action of dry ammonia on sulphur chloride dissolved in benzene. This substance corresponds with cyanogen (paracyanogen), and is known as **nitrogen sulphide**. It is formed according to the equation: $3SCl_2 + 8NH_3 = N_2S_2 + S + 6NH_4Cl$. The free sulphur and nitrogen sulphide are dissolved by acting on the product with carbon bisulphide, the nitrogen sulphide being much less soluble than the sulphur. It is a yellow substance, which is excessively irritating to the eyes and nostrils. It explodes when rubbed with a hard substance, being naturally decomposed with the evolution of nitrogen; but when heated it fuses without decomposing, and only decomposes with explosion at 157°. It is insoluble in water, and only slightly so in alcohol, ether, and carbon bisulphide; 100 parts of the latter dissolve 1·5 part of nitrogen sulphide at the boiling-point. This solution on cooling deposits the sulphide in minute transparent prisms of a golden yellow colour.

A mixture of S_4N_4 and chloroform gives a precipitate of $S_4N_4Cl_4$ when treated with chlorine (Demarçay, Muthmann, and others), and S_4N_3Cl when treated with a chloroform solution of S_2Cl_2. The latter compound has the appearance of golden scales which dissolve in water with difficulty, but are soluble in strong nitric acid, forming, when evaporated *in vacuo*, an explosive substitution product, $S_4N_3NO_3$, as large yellow crystals which are soluble in water, but readily decompose. In general Muthmann and Seitter (1897) obtained a series of compounds, S_4N_3X, apparently of a saline character. Their relation to other compounds of S and N cannot yet be regarded as clear. If a solution of S_4N_3Cl in methyl alcohol is treated (until it turns red) with zinc dust, it (Muthmann and Clever, 1896) forms **nitrogen pentasulphide**, N_2S_5 (in some respects the analogue of N_2O_5), which is a remarkable substance in many ways, although not evincing the character of a thio-acid anhydride with any clearness. It is obtained by heating a solution of three parts of S_4N_4 in fifty parts of CS_2 in a closed vessel (five atmospheres pressure) at 100° for some time. On evaporating the filtrate it deposits sulphur and a dark-red strongly smelling oil, which is purified by dissolving it in ether and, when pure, fuses at about 10° and resembles iodine in its appearance. It decomposes when heated, forms NH_3 with water, and is apparently formed together with free cyanogen sulphide: $S_4N_4 + 2CS_2 = S + (CNS)_2 + N_2S_5$. Its alcoholic solution is violet. If the compounds spoken of in note 40 be added to the above nitrogen compounds of sulphur, it will be seen how varied may be the combinations of elements, like sulphur, able to form compounds of two types RX_5—like nitrogen and RX_6.

H_2, forming H_2O, H_2S, H_2Se, and H_2Te.[78b] The hydrogen compounds of selenium and tellurium are acids like hydrogen sulphide. Selenium, by simple heating in a stream of hydrogen, partially combines with it directly, but seleniuretted hydrogen is more readily decomposable by heat than sulphuretted hydrogen, and this property is still more developed in telluretted hydrogen. Hydrogen selenide and telluride are gases like sulphuretted hydrogen, and, like it, are soluble in water, form saline compounds with alkalies, precipitate metallic salts, are obtained by the action of acids on their compounds with metals, &c. Selenium and tellurium, like sulphur, give two normal grades of combination with oxygen, both of an acid character, of which only the forms corresponding to sulphurous anhydride—namely, selenious anhydride, SeO_2, and tellurous anhydride, TeO_2[79]—are formed directly.

[78b] Telluretted hydrogen, TeH_2, was obtained (Davy) by electrolysis, by the action of HCl on an alloy of tellurium and zinc, and by the action of water or dilute acids on Al_2Te_3 (Engel, Forcrand, and others). It is a very unstable colourless gas, which colours solutions of the alkalies red, and liquefies at about 0° into a liquid of sp. gr. 2·5 which freezes at about −50°. It forms unstable compounds with metals.

[79] **Selenious anhydride**, SeO_2, is a volatile (at about 320°) solid, which crystallises in prisms soluble in water. It is best procured by the action of nitric acid on selenium. The well-known researches of Nilson (1874) showed that the salts of selenious acid readily form acid salts, and are so characteristic in many respects that they may even serve for judging the analogy of types of oxides. Thus, the oxides of the composition RO give normal salts of the composition $RSeO_3,2H_2O$, where R = Mn, Co, Ni, Cu, Zn. The salts of magnesium, barium, and calcium contain a different quantity of water, as also do the salts of the oxides R_2O_3. We may here turn attention to the fact that beryllium gives a normal salt, $BeSeO_3,2H_2O$, and not a salt analogous to those of aluminium, scandium, $Sc_2(SeO_3)_3,H_2O$, yttrium, $Y_2(SeO_3)_3,12H_2O$, and other oxides of the form R_2O_3, which speaks in favour of the formula BeO.

Tellurous anhydride is also a colourless solid, which crystallises in octahedra: it also, when heated, first fuses and then volatilises. It is insoluble in water, and the decomposition of its salts gives a hydrate, H_2TeO_3, which is insoluble.

It is a very characteristic circumstance that selenious and tellurous anhydrides are very easily **reduced** to selenium and tellurium. This is not only effected by metals like zinc, or by sulphuretted hydrogen, which are powerful deoxidisers, but even by sulphurous anhydride, which is able to precipitate selenium and tellurium from solutions of the selenites and tellurites, and even of the acids themselves, which is taken advantage of in obtaining these elements and separating them from sulphur.

Sulphuric acid, as we know, rarely acts as an oxidising agent. It is otherwise with selenic and telluric acids, H_2SeO_4 and H_2TeO_4, which are powerful oxidising agents—that is, are easily reduced in many circumstances either into the lower oxide or even to selenium and tellurium. A powerful oxidising agent is required in order to convert selenious and tellurous anhydrides into selenic and telluric anhydrides, and, moreover, it must be employed in excess. If chlorine is passed through a solution of potassium selenide, K_2Se, telluride, K_2Te, selenite, K_2SeO_3, or tellurite, K_2TeO_3, it acts as an oxidiser in the presence of the water, forming potassium selenate, K_2SeO_4, or tellurate, K_2TeO_4. The same salts are formed by fusing the lower oxides with nitre. These salts are isomorphous with the corresponding sulphates, and cannot therefore be separated from them by crystallisation. The salts of potassium, sodium, magnesium, copper, cadmium, &c., are soluble like the sulphates, but those of barium and calcium are insoluble, in perfect analogy with the sulphates. When copper selenate, $CuSeO_4$, is treated with sulphuretted hydrogen (CuS

In distinction from sulphur these are both solids, obtained by the combustion of the elements themselves, like SO_2, and by the action of oxidising agents on them. They form feebly energetic acids, having distinct dibasic properties; however a characteristic difference from SO_2 is observable, not so much in the physical properties of these compounds, as in their stability and capacity for further oxidation, just as in the series of the halogens already known to us, only in an inverse order; in the latter we saw that iodine combines more easily than bromine or chlorine with oxygen, forming more stable oxygen compounds, whereas, on the contrary, selenious and tellurous anhydrides are oxidised with difficulty and easily reduced, even by means of sulphurous acid.

Selenium was obtained in 1817 by Berzelius from the sublimate which collects in the first chamber in the preparation of sulphuric acid from Fahlun pyrites. Certain other pyrites also contain small

---

is precipitated), **selenic acid** remains in solution. On evaporation and drying *in vacuo* at 180°, it gives a syrupy liquid, which may be concentrated to almost the pure acid, H_2SeO_4, having a specific gravity of 2·6. Cameron and Macallan (1891) showed that pure H_2SeO_4 only remains liquid in a state of superfusion, whilst the solidified acid melts at +58°; the solid acid crystallises well, its sp. gr. being then 2·95. The hydrate H_2SeO_4,H_2O melts at +25°. The acid in a superfused state has a sp. gr. 2·36, that of the solid being 2·68. Like sulphuric acid, strong selenic acid attracts moisture from the atmosphere; it is not decomposed by sulphurous acid, but oxidises hydrochloric acid (like nitric, chromic, and manganic acids), evolving chlorine and forming selenious acid, $H_2SeO_4 + 2HCl = H_2SeO_3 + H_2O + Cl_2$. **Telluric acid**, H_2TeO_4, is obtained by fusing tellurous anhydride with potassium hydroxide and chlorate; the solution, containing potassium tellurate, is then precipitated with barium chloride, and the barium tellurate, $BaTeO_4$, obtained in the precipitate is decomposed by sulphuric acid. A solution of telluric acid is thus obtained, which on evaporation yields colourless prisms soluble in water, and of the composition $TeH_2O_4,2H_2O$. These two equivalents of water are driven off at 160°; on further heating the last equivalent of water is expelled, and then oxygen is given off. It also gives chlorine with hydrochloric acid, like selenic acid. Its salts also correspond with those of sulphuric acid. It must, however, be remarked that telluric and selenic acids are able to give poly-acid salts with much greater ease than sulphuric acid. Thus, for example, there are known for telluric acid not only $K_2TeO_4,5H_2O$ and $KHTeO_4,3H_2O$, but also $KHTeO_4,H_2TeO_4,H_2O = K_2TeO_4,3H_2TeO_4,2H_2O$. This salt is easily obtained from acid solutions of the preceding salts, and is less soluble in water. As selenious anhydride is volatile and gives similar poly-salts, it may be surmised that selenious, tellurous, selenic, and telluric anhydrides are polymeric as compared with sulphurous and sulphuric anhydrides, for which reason it would be desirable to determine the vapour density of selenious anhydride. It would probably correspond with Se_2O_4 or Se_3O_6.

In order to show the very close analogy of selenium to sulphur, I shall quote two examples. Potassium cyanide dissolves selenium, as it does sulphur, forming potassium selenocyanate, KCNSe, corresponding with potassium thiocyanate. Acids precipitate selenium from this solution, because selenocyanic acid, HCNSe, when in a free state is immediately decomposed. A boiling solution of sodium sulphite dissolves selenium, just as it would sulphur, forming a salt analogous to thiosulphate of sodium, namely, sodium selenosulphate, Na_2SSeO_3. Selenium is separated from a solution of this salt by the action of acid.

quantities of selenium. Some native selenides, especially those of lead, mercury, and copper, have been found in the Hartz Mountains, but only in small quantities. Pyrites and blendes, in which the sulphur is partially replaced by selenium, still remain the chief source for its extraction. When these pyrites are roasted they evolve selenious anhydride, which condenses in the cooler portions of the roasting apparatus, and is partially or wholly reduced by the sulphurous anhydride simultaneously formed. The presence of selenium in ores and sublimates is most simply tested by heating them before the blowpipe, when they evolve the characteristic odour of garlic. Selenium exhibits two modifications, like sulphur: one amorphous and insoluble in carbon bisulphide, the other crystalline and slightly soluble in carbon bisulphide (in 1,000 parts at 45° and 6,000 at 0°), and separating from its solutions in monoclinic prisms. If the red precipitate obtained by the action of sulphurous anhydride on selenious anhydride is dried, it gives a brown powder, having a specific gravity of 4·26, which when heated changes colour and fuses to a metallic mass, becoming lustrous as it cools. The selenium acquires different properties according to the rate at which it is cooled from a fused state; if rapidly cooled, it remains amorphous and has the same specific gravity (4·28) as the powder; but if slowly cooled it becomes crystalline and opaque, soluble in carbon bisulphide, and has a specific gravity of 4·80. In this form it fuses at 214° and remains unchanged, whilst the amorphous form, especially above 80°, gradually passes into the crystalline variety. The transition is accompanied by the evolution of heat, as in the case of sulphur; so that the analogy between sulphur and selenium is here clearly shown. In the fused amorphous form, selenium presents a brown mass, slightly translucent, with a vitreous fracture, whilst in the crystalline form it has the appearance of a grey metal, with a feeble lustre and a crystalline fracture.[79a] Selenium boils at 700°, forming a vapour the density of which is only constant at a temperature of about 1400°, when it is equal to 79·4 (referred to hydrogen)—that is, the molecular formula is Se_2, as with sulphur at an equally high temperature.

Tellurium is met with still more rarely than selenium (in Saxony)

[79a] Muthmann, in his researches on the allotropic forms of selenium, pointed out (1889) a peculiar modification, which appears, as it were, as a transition between crystalline and amorphous selenium. It is obtained together with the crystalline variety by slowly evaporating a solution of selenium in bisulphide of carbon, and differs from the crystalline variety in the form of its crystals; it passes into the latter modification when heated. Schultz (1885) and subsequently Gutbier (1902) also obtained selenium (like Ag; see Chap. XXIV.) in a soluble form by the interaction of dilute solutions of SeO_2 and hydrate of hydrazine; but these researches are not so conclusive as those upon soluble silver, and we shall therefore not consider them more fully. Tellurium has also been obtained in a soluble colloidal state.

in combination with gold, silver, lead, and antimony in the so-called foliated tellurium ore. Bismuth telluride and silver telluride have been found in Hungary and in the Altai. Tellurium is extracted from bismuth telluride by mixing the finely powdered ore with potassium and charcoal in as intimate a mixture as possible, and then heating in a covered crucible. Potassium telluride, K_2Te, is then formed, because the charcoal reduces potassium tellurite. As potassium telluride is soluble in water, forming a red-brown solution, which is decomposed by the oxygen of the atmosphere ($K_2Te + O + H_2O = 2KHO + Te$), the mass formed in the crucible is treated with boiling water and filtered as rapidly as possible, and the resultant solution exposed to the air, by which means the tellurium is precipitated.[80] In a free state tellurium has a perfectly metallic appearance; it is of a silver-white colour, crystallises very easily in long brilliant needles, is very brittle, so that it can be easily reduced to powder, but is a bad conductor of heat and electricity, and in this respect, as in many others, it forms a transition from the metals to the non-metals. Its specific gravity is 6·18, it melts at an incipient red heat, and takes fire when heated in air, like selenium and sulphur, burning with a blue flame, evolving white fumes of tellurous anhydride, TeO_2, and emitting an acrid smell if no selenium is present; but if it contains selenium, the odour of the latter preponderates. Alkalies dissolve tellurium when boiled with it, potassium telluride, K_2Te, and potassium tellurite, K_2TeO_3, being formed. The solution is of a red colour, owing to the presence of the telluride, K_2Te; but the

---

[80] The tellurium thus prepared is impure, and contains a large amount of selenium. The latter may be removed by converting the mixture into the salts of potassium and treating these with nitric acid and barium nitrate, when barium selenate only is precipitated, whilst the barium tellurate remains in solution. This method does not, however, give a pure product, and it appears to be best to separate the selenium from the tellurium in a metallic form; this is done by boiling the impure potassium tellurate with hydrochloric acid, which converts it into potassium tellurite, from which the tellurium is reduced by sulphurous anhydride. The metal thus obtained is then fused and distilled in a stream of hydrogen; the selenium volatilises first, and then the tellurium, which is much less volatile than the former. Nevertheless, tellurium is also volatile, and may be separated in this manner from less volatile metals, such as antimony. Brauner showed (1889) that tellurium purified by the usual method, even after distillation, contains a large amount of impurities. The atomic weight of Te has been the object of repeated investigation; and although in recent years (1889–1902) many (Brauner, Mether, Chikashigé, Köthner, Pellini, Gutbier, and others) have found it to lie between 127·8 and 127·9 ($O = 16$), the mean being 127·7, i.e., greater than that of iodine (about 126·9), yet Steiner (1901) by analysing the volatile $(C_6H_5)_2Te$, found $Te = 126·4$, which is less than for iodine. My personal opinion is that the atomic weights of iodine (see Chap. XI., note 62) and tellurium are very near 127 ($O = 16$), and that only experiment and very careful fresh researches can prove which is the greater, although it *seems* to me more probable that I is slightly greater than Te, as it should be according to the periodic law, and that the iodine experimented on contained traces of Cl and Br, and that its atomic weight is greater than 127. This question must be decided by future investigators.

colour disappears when the solution is cooled or diluted, the tellurium being all precipitated: $2K_2Te + K_2TeO_3 + 3H_2O = 6KHO + 3Te$.[81]

---

[81] The decomposition proceeds in the above order in the cold, but in a hot solution with an excess of potassium hydroxide it proceeds inversely. A similar phenomenon takes place when tellurium is fused with alkalies, and it is therefore necessary in order to obtain potassium telluride to add charcoal.

Selenium and tellurium form higher compounds with chlorine with comparative ease. For selenium, $SeCl_2$ and $SeCl_4$ are known, and for tellurium $TeCl_2$ and $TeCl_4$. The tetrachlorides of selenium and tellurium are formed by passing chlorine over these elements. Selenium tetrachloride, $SeCl_4$, is a crystalline volatile mass which gives selenious anhydride and hydrochloric acid with water. Tellurium tetrachloride is much less volatile, fuses easily, and is also decomposed by water. Both elements form similar compounds with bromine. Tellurium tetrabromide is red, fuses to a brown liquid, volatilises, and gives a crystalline salt, $K_2TeBr_6,3H_2O$, with an aqueous solution of potassium bromide.

CHAPTER XXI

CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM, AND MANGANESE

SULPHUR, selenium, and tellurium belong to the uneven series of the sixth group. In the even series of this group there are known **chromium, molybdenum, tungsten**, and **uranium**; these give oxides of the type RO_3, like SO_3. Their acid properties are less sharply defined than those of sulphur, selenium, and tellurium, as is the case with all elements of the even series as compared with those of the uneven series in the same group. But still the oxides CrO_3, MoO_3, WO_3, and even UO_3, form salts of the composition MO,nRO_3 with bases MO. In the case of the heavy elements, and especially of uranium, the type of oxide, UO_3, is less acid and more basic, because in the even series of oxides the element with the highest atomic weight always acquires a more and more pronounced basic character. Hence UO_3 shows the properties of a base, and gives salts, UO_2X_2. The basic properties of chromium, molybdenum, tungsten, and uranium are most clearly expressed in the lower oxides, which they all form. Thus chromic oxide, Cr_2O_3, is as distinct a base as alumina, Al_2O_3.

Of all these elements **chromium** is the most widely distributed in nature and the most frequently used. It gives chromic anhydride, CrO_3, and chromic oxide, Cr_2O_3—two compounds whose relative amounts of oxygen stand in the ratio 2 : 1. Chromium is, although somewhat rarely, met with in nature as a compound of one or the other type. The red chromium ore of the Urals, lead chromate or crocoisite, $PbCrO_4$, was the source in which chromium was discovered by Vauquelin, who gave it this name (from the Greek word χρῶμα, signifying colour) owing to the brilliant colours of its compounds; the chromates (salts of chromic anhydride) are red and yellow, and the chromic salts (from Cr_2O_3), green and violet. The red lead chromate is, however, very rare. Chromic oxide, Cr_2O_3, is more frequently met with. In small quantities it forms the colouring matter of many minerals and rocks—for example, of some serpentines. The commonest ore, and the chief source of the chromium compounds, is **chrome iron ore**, or chromite, which occurs in the

Urals[1] and Asia Minor, California, Australia, and other localities. This is magnetic iron ore, FeO,Fe_2O_3, in which the ferric oxide is replaced by chromic oxide, its composition being FeO,Cr_2O_3. Chrome iron ore crystallises in octahedra of sp. gr. 4·4 ; it has a feeble metallic lustre, is of a greyish-black colour, and gives a brown powder. It is very feebly acted on by acids, but when fused with acid potassium sulphate it gives a soluble mass, which contains a chromic salt, besides potassium and ferrous sulphates. In practice the treatment of chrome iron ore is mainly carried on for the preparation of chromates, and not of chromic salts, and therefore we shall trace the history of the element by beginning with chromic acid, and especially with the working up of the chrome iron ore into **potassium dichromate**, $K_2Cr_2O_7$, as the most common salt of this acid. It must be remarked that chromic anhydride, CrO_3, is only obtained in an anhydrous state, and is distinguished for its capacity for easily giving anhydro-salts with the alkalies, containing one, two, and even three equivalents of the anhydride to one equivalent of base. Thus, among the potassium salts there is known the normal or yellow chromate, K_2CrO_4, which corresponds to, and is perfectly isomorphous with, potassium sulphate. As in the presence of a certain excess of acid,the dichromate ($K_2Cr_2O_7=2K_2CrO_4+2HX-2KX-H_2O$) is easily formed from K_2CrO_4, the object of the manufacturer is to produce such a dichromate, the more so as it contains a larger proportion of the elements of chromic acid than the normal salt. Finely ground chrome iron ore, when heated with an alkali, absorbs oxygen almost as easily (Chap. III., note 7) as a mixture of the oxides of manganese with an alkali. The chromic oxide is oxidised into the anhydride, $Cr_2O_3+O_3=2CrO_3$, and then combines with the alkali. As the oxidation and formation of the chromate proceed, the mass turns *yellow*. The iron is also oxidised, forming Fe_2O_3.

A mixture of lime (sometimes with potash) and chrome iron ore is heated in a reverberatory furnace, with free access of air and at a red heat for several hours, until the mass becomes yellow ; it then contains normal calcium chromate, $CaCrO_4$, which is insoluble in water in the presence of an excess of lime.[1a] The resultant mass is ground up, and treated with water and sulphuric acid. The excess of lime forms gypsum, and the soluble calcium dichromate, $CaCr_2O_7$, together with a certain amount of iron, passes into solution. The solution is poured off

---

[1] The working of the Ural chrome iron ore into chromium compounds has been firmly established in Russia, thanks to the endeavours of P. K. Ushkoff, who constructed large works for this purpose on the river Kama, near Elabougi.

[1a] But the calcium chromate is soluble in water in the presence of an excess of chromic acid, as may be seen from the fact that a solution of chromic acid dissolves lime.

and chalk added to it; this precipitates the ferric oxide and forms a fresh quantity of gypsum, while the chromic acid remains in solution—that is, it does not form the sparingly soluble normal salt (1 part soluble in 240 parts of water). The solution then contains a fairly pure calcium dichromate, which by double decomposition gives other chromates; for example, with a solution of potassium sulphate it gives a precipitate of calcium sulphate and a solution of potassium dichromate, which crystallises when evaporated.[2]

Potassium dichromate, $K_2Cr_2O_7$, readily crystallises from acid solutions in red, well-formed prismatic crystals, which fuse at a red heat and evolve oxygen at a very high temperature, leaving chromic oxide and the normal salt, which undergoes no further change: $2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + O_3$. At the ordinary temperature 100 parts of water dissolve 10 parts of this salt, and the solubility increases as the temperature rises. It is most important to note that the dichromate does not contain water; it is $K_2CrO_4 + CrO_3$; the acid salt corresponding to acid potassium sulphate, $KHSO_4$, does not exist. In dissolving in water, it produces cold, i.e., it does not form a very stable compound with water. The solution and the salt itself are poisonous, and act as powerful oxidising agents, which is the character of chromic acid in general. When heated with sulphur or organic substances, with sulphurous anhydride, hydrogen sulphide, &c., this salt is deoxidised, yielding chromic compounds.[2a] Potassium dichromate[3] is used in the

---

[2] There are many variations in the details of the manufacturing processes, and these must be looked for in works on technical chemistry. But we may add that the chromate may also be obtained by slightly roasting briquettes of a mixture of chrome iron and lime and then leaving the resultant mass to the action of moist air (oxygen is absorbed, and the mass turns yellow). The sodium salt, $Na_2Cr_2O_7,2H_2O$, is now most frequently used in practice. It dissolves readily in water.

[2a] The oxidising action of potassium dichromate on organic substances at the ordinary temperature is especially marked under the action of light. Thus it acts on gelatin, as Poutven discovered; this is applied to photography in the processes of photogravure, photo-lithography, pigment printing, &c. Under the action of light this gelatin is oxidised (and the chromic anhydride deoxidised), forming a compound insoluble in warm water, whilst where the light has not acted, the gelatin remains soluble, its properties being unaffected by the presence of chromic acid or potassium dichromate. A mixture of $Na_2Cr_2O_7$ with a small quantity of glycerine takes fire when heated to 100°, leaving a pulverulent mass of oxide of chromium; the glycerine is oxidised.

[3] Ammonium and sodium dichromates are now also prepared on a large scale. The sodium salts may be prepared in exactly the same manner as those of potassium. The normal salt crystallises with ten equivalents of water, like Glauber's salt, with which it is isomorphous. Its solution above 80° deposits the anhydrous salt. Sodium dichromate crystals have the composition $Na_2Cr_2O_7,2H_2O$. **The ammonium salts of chromic acid** are obtained by saturating the anhydride itself with ammonia. The dichromate is obtained by saturating one part of the anhydride with ammonia and then adding a second part of anhydride and evaporating under the receiver of an air-pump. On ignition, the ammonium salts leave chromic oxide. Potassium ammonium chromate, NH_4KCrO_4, is

arts and in chemistry as a source for the preparation of all other chromium compounds. It is converted into yellow pigments by means of double decomposition with salts of lead, barium, and zinc. When solutions of the salts of these metals are mixed with potassium dichromate (in dyeing generally mixed with soda, in order to obtain normal salts), they are precipitated as insoluble normal salts; for example, $2BaCl_2 + K_2Cr_2O_7 + H_2O = 2BaCrO_4 + 2KCl + 2HCl$. It follows from this that these salts are insoluble in dilute acids, but the precipitation is not complete (as it would be with the normal salt). The barium and zinc salts are of a lemon-yellow colour; the lead salt has a still more intense colour, passing into orange. Yellow cotton prints are dyed with this pigment. The silver salt, Ag_2CrO_4, is of a bright-red colour.

When potassium dichromate is mixed with potassium hydroxide or carbonate (carbonic anhydride being disengaged in the latter case) it forms the **normal** salt, K_2CrO_4, known as **yellow chromate of potassium.** Its specific gravity is 2·7, being almost the same as that of the dichromate. It absorbs heat in dissolving; one part of the salt dissolves in 1·75 part of water at the ordinary temperature, forming a yellow solution. When mixed with even such feeble acids as acetic, and more especially with the ordinary acids, it gives the dichromate, and Graham obtained a trichromate, $K_2Cr_3O_{10} = K_2CrO_4,2CrO_3$, by mixing a solution of the dichromate with an excess of nitric acid.

---

obtained in yellow needles from a solution of potassium dichromate in aqueous ammonia; it loses ammonia and becomes converted into potassium dichromate not only when ignited, but also by degrees at the ordinary temperature. This shows the feeble energy of chromic acid, and its tendency to form stable dichromates. Magnesium chromate is soluble in water, as also is the strontium salt. The calcium salt is also somewhat soluble, but the barium salt is almost insoluble. The isomorphism with sulphuric acid is shown in the chromates by the fact that the magnesium and ammonium salts form double salts containing six equivalents of water, which are perfectly isomorphous with the corresponding sulphates. The magnesium salt crystallises in large crystals containing seven equivalents of water. The beryllium, cerium, and cobalt salts are insoluble in water. Chromic acid dissolves manganous carbonate, but on evaporation the solution deposits manganese dioxide, formed at the expense of the oxygen of the chromic acid. Chromic acid also oxidises ferrous oxide, and the hydroxide is soluble in chromic acid.

One of the chromates most used by the dyer is the insoluble yellow lead chromate, $PbCrO_4$ (Chap. XVIII., note 46), which is precipitated on mixing solutions of PbX_2 with soluble chromates. It easily forms a basic salt, having the composition $PbO,PbCrO_4$, as a crystalline powder, obtained by fusing the normal salt with nitre and then rapidly washing in water. The same substance is obtained, although impure and in small quantity, by treating lead chromate with neutral potassium chromate, especially on boiling the mixture; and this gives the possibility of attaining, by means of these materials, various tints of lead chromate, from yellow to red, passing through different shades of orange. The decomposition which takes place (incompletely) in this case is as follows: $2PbCrO_4 + K_2CrO_4 = PbCrO_4,PbO + K_2Cr_2O_7$—that is, potassium dichromate is formed in solution. A hot solution of $AgNO_3$ and K_2CrO_4 in the presence of nitric acid gives dichromate of silver, $Ag_2Cr_2O_7$, in the form of a crystalline precipitate, which is decomposed by water into $Ag_2CrO_4 + CrO_3$ (Autenrieth).

Chromic anhydride is obtained by preparing a saturated solution of potassium dichromate at the ordinary temperature and pouring it in a thin stream into an equal volume of pure sulphuric acid.[4] On mixing, the temperature naturally rises; when slowly cooled, the solution deposits chromic anhydride in red needle-shaped crystals, sometimes several centimetres long. The crystals are freed from the mother liquor by placing them on a porous tile.[4a] It is very important at this point to call attention to the fact that a hydrate of chromic anhydride is never obtained in the decomposition of chromic compounds, but always the **anhydride,** CrO_3. The corresponding hydrate, CrO_4H_2, or any other hydrate, is not even known. Nevertheless, it must be admitted that chromic acid is dibasic, because it forms salts isomorphous or perfectly analogous with the salts formed by sulphuric acid, which is the best example of a dibasic acid. A proof of this is seen in the fact that the anhydride and salts give (when heated with sodium chloride and sulphuric acid) a volatile chloranhydride, CrO_2Cl_2, containing two atoms of chlorine, as a dibasic acid should.[5] Chromic anhydride is a red

---

[4] The sulphuric acid should not contain any lower oxides of nitrogen, because these reduce chromic anhydride to chromic oxide. If a solution of a chromate is heated with an excess of acid—for instance, sulphuric or hydrochloric acid—oxygen or chlorine is evolved, and a solution of a chromic salt is formed. One of the first methods by which CrO_3 was obtained consisted in converting its salts into volatile **chromium hexafluoride,** CrF_6. This compound was obtained by Unverdorben by mixing lead chromate with fluor spar in a dry state and treating the mixture with fuming sulphuric acid in a platinum vessel: $PbCrO_4 + 3CaF_2 + 4H_2SO_4 = PbSO_4 + 3CaSO_4 + 4H_2O + CrF_6$. Chromium fluoride is volatile, and forms a very caustic, poisonous vapour, which condenses when cooled in a dry platinum vessel into a red exceedingly volatile liquid, fuming strongly in the air. The vapours of this substance when introduced into water are decomposed into hydrofluoric acid and chromic anhydride: $CrF_6 + 3H_2O = CrO_3 + 6HF$. If very little water is taken the hydrofluoric acid volatilises, and chromic anhydride separates directly in crystals. The chloranhydride of chromic acid, CrO_2Cl_2 (note 5), is also decomposed in the same manner. A solution of chromic acid and a precipitate of barium sulphate are formed by treating the insoluble barium chromate with an equivalent quantity of sulphuric acid. If carefully evaporated, the solution yields crystals of chromic anhydride. Fritzsche gave a very convenient method of preparing chromic anhydride, based on the relation of chromic to sulphuric acid. At the ordinary temperature the strong acid dissolves both chromic anhydride and potassium chromate, but if a certain amount of water is added to the solution the chromic anhydride separates, and if the amount of water is increased the precipitated chromic anhydride is again dissolved. The chromic anhydride is almost all separated from the solution when it contains two equivalents of water to one of sulphuric acid.

[4a] They cannot be filtered through paper or washed, because the chromic anhydride is reduced by the filter paper, and is dissolved during the process of washing.

[5] Berzelius observed, and Rose carefully investigated, this remarkable reaction, which occurs between chromic acid and sodium chloride in the presence of sulphuric acid. If 10 parts of common salt are mixed with 12 parts of potassium dichromate, fused, cooled, broken up into lumps, and covered with 20 parts of fuming sulphuric acid, it gives rise to a violent reaction, accompanied by the formation of brown fumes of **chromic chloranhydride,** or **chromyl chloride,** CrO_2Cl_2, according to the reaction: $CrO_3 + 2NaCl + H_2SO_4 = Na_2SO_4 + H_2O + CrO_2Cl_2$. The addition of an excess of sulphuric acid is

crystalline substance, which is converted into a black mass by heat; it fuses at 190°, and disengages oxygen above 250°, leaving a residue of chromium dioxide, CrO_2,[6] and, on still further heating, chromic oxide, Cr_2O_3. Chromic anhydride is exceedingly soluble in water, and even attracts moisture from the air; but, as was mentioned above, it does not form any definite compound with water. The specific gravity of its crystals is 2·7, and when fused it has a specific gravity 2·6. The solution presents perfectly defined acid properties. It liberates carbonic anhydride from carbonates; gives insoluble precipitates of the chromates with salts of barium, lead, silver, and mercury.

necessary in order to retain the water. The same substance is always formed when a metallic chloride is heated with chromic and sulphuric acids. With CrO_3, a strong solution of HCl or gaseous HCl directly forms water and CrO_2Cl_2, but this compound is decomposed by an excess of water. The formation of this volatile substance is easily observed, owing to the brown colour peculiar to its vapour. On condensing the vapour in a dry receiver, a liquid is obtained having a sp. gr. of 1·9, boiling at 118°, and having the vapour density 78, which corresponds with the above formula. Chromyl chloride is decomposed by heat into chromic oxide, oxygen, and chlorine: $2CrO_2Cl_2 = Cr_2O_3 + 2Cl_2 + O$; so that it is able to act simultaneously as a powerful oxidising and chlorinating agent. When brought into contact with inflammable substances it often sets fire to them; for instance, phosphorus, sulphur, oil of turpentine, ammonia, hydrogen, and other substances. It attracts moisture from the atmosphere with great energy, and must therefore be kept in closed vessels. It dissolves iodine and chlorine, and even forms a solid compound with the latter, which depends upon the faculty of chromium to form its higher oxide, Cr_2O_7. The close analogy in physical properties of the chloranhydrides, CrO_2Cl_2 and SO_2Cl_2, is very remarkable, although sulphurous anhydride is a gas, and the oxide, CrO_2 (which is mentioned in the following note), a non-volatile solid.

If three parts of potassium dichromate are mixed with four parts of strong hydrochloric acid and a small quantity of water, and gently warmed, it all passes into solution, and no chlorine is evolved; on cooling, the liquid deposits red prismatic crystals, known as **Peligot's salt**, very stable in air. This has the composition KCl,CrO_3, and is formed according to the equation, $K_2Cr_2O_7 + 2HCl = 2KCl,CrO_3 + H_2O$. It is evident that this is the first chloranhydride of chromic acid, $HCrO_3Cl$, in which the hydrogen is replaced by potassium. It is decomposed by water, and on evaporation the solution yields potassium dichromate and hydrochloric acid. This is a fresh instance of the reversible reactions so frequently encountered. With sulphuric acid Peligot's salt forms chromyl chloride. Geuther produced Peligot's salt from potassium chromate and chromyl chloride. When heated, it parts with all its chlorine, and on further heating gives chromic oxide.

[6] This dioxide, CrO_2, may also be obtained by mixing solutions of chromic salts with solutions of chromates. The brown precipitate formed contains a compound, Cr_2O_3,CrO_3, consisting of equivalent amounts of chromic oxide and anhydride. The brown precipitate of chromium dioxide contains water. The same substance is formed by the imperfect deoxidation of chromic anhydride by various reducing agents. Chromic oxide, when heated, absorbs oxygen, and appears to give the same substance. Chromic nitrate, when ignited, gives CrO_2. When CrO_2 is ignited it disengages oxygen, chromic oxide being left. It is the analogue of manganese dioxide. Krüger treated chromium dioxide with a mixture of sodium chloride and sulphuric acid, and found that chlorine gas was evolved, but that chromyl chloride was not formed. Under the action of light, a solution of chromic acid also deposits the brown dioxide. At the ordinary temperature chromic anhydride leaves a brown stain upon the skin and tissues, which probably proceeds from a decomposition of the same kind. Chromic anhydride is soluble in alcohol containing water, and this solution is decomposed in a similar manner by light. Chromium dioxide forms K_2CrO_4 when treated with H_2O_2 in the presence of KHO.

The action of hydrogen peroxide on a solution of chromic acid or of potassium dichromate gives a blue solution, which very quickly becomes colourless with the disengagement of oxygen. Barreswill showed that this is due to the formation of a **perchromic anhydride**, Cr_2O_7. This peroxide is remarkable from the fact that it very easily dissolves in ether and is much more stable in this solution, so that, by shaking up hydrogen peroxide mixed with a small quantity of chromic acid with ether, it is possible to transfer all the blue substance formed to the ether.[6a]

When heated with oxygen acids, chromic acid evolves oxygen ; for example, with sulphuric acid the following reaction takes place : $2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + O_3 + 3H_2O$. It will be readily understood from this that **a mixture of chromic acid** or **of its salts with sulphuric acid** forms an excellent **oxidising agent**, which is frequently employed in chemical laboratories and for technical purposes as a means of oxidation. Thus hydrogen sulphide and sulphurous anhydride are converted into sulphuric acid by this means. Chromic acid is able to act as a powerful oxidising agent because it passes into chromic oxide, and in so doing disengages half of the oxygen contained in it : $2CrO_3 = Cr_2O_3 + O_3$.[6b] In acting on a solution of potassium iodide, CrO_3, like many other oxidising agents, liberates iodine ; the reaction proceeds in proportion to the amount of CrO_3 present, and may serve for determining the amount of CrO_3, since the quantity of iodine liberated can be accurately determined by the iodometric method (Chap. XX., note 42). If chromic anhydride be ignited in a stream of ammonia, it gives chromic oxide, water, and nitrogen. In all cases when chromic acid acts as an oxidising agent in the presence of acids and under the action of heat, the product of its deoxidation is a chromic salt, CrX_3, which is green, so that the **red** or yellow **solution** of a salt of chromic acid is then transformed into a **green** solution of a chromic salt, derived from chromic oxide, Cr_2O_3, which is analogous to Al_2O_3, Fe_2O_3, and

---

[6a] It might be supposed that perchromic anhydride, Cr_2O_7, would correspond to perchromic acid, $H_2Cr_2O_8$, but as yet it is not certain whether corresponding salts are formed. Péchard (1891), on adding an excess of H_2O_2 and baryta water to a dilute solution of CrO_3 (8 grms. per litre), observed the formation of a yellow precipitate; but oxygen was disengaged at the same time, and the precipitate (which easily exploded when dried) was found to contain, besides an admixture of BaO_2, a compound, $BaCrO_5$, and this ($BaO_2 + CrO_3$) does not correspond with perchromic acid.

[6b] Thus, chromic anhydride itself is a powerful oxidising agent, and is therefore employed instead of nitric acid in galvanic batteries (as a depolariser), the hydrogen evolved at the carbon being then oxidised, and the chromic acid converted into a non-volatile product of deoxidation, instead of yielding, as nitric acid does, volatile lower oxides of offensive odour. Organic substances are more or less perfectly oxidised by means of chromic anhydride, although this generally requires the aid of heat, and does not proceed in the presence of alkalies, but generally *in the presence of acids.*

other bases of the composition R_2O_3. This analogy is seen in the insolubility of the anhydrous oxide, in the gelatinous form of the colloidal hydrate, in the formation of alums[7] and of a volatile anhydrous

[7] As a mixture of potassium dichromate and sulphuric acid is usually employed for oxidation, the resultant solution generally contains a double sulphate of potassium and oxide of chromium—that is, **chrome alum**, $KCr(SO_4)_2,12H_2O$. It is prepared by dissolving potassium dichromate in dilute sulphuric acid; alcohol is then added and the solution slightly heated (aldehyde, C_2H_4O, is disengaged) or sulphurous anhydride is passed through it. If the temperature of decomposition does not exceed 35°, a **violet** solution of chrome alum is obtained, but if the solution is heated, a solution of the same alum is obtained of a **green** colour. As chrome alum requires for solution 7 parts of water at the ordinary temperature, it follows that if a somewhat strong solution be taken, chrome alum will separate out on cooling. **If the liquid be heated** somewhat strongly, for instance, to the boiling-point of water, it acquires a bright **green colour**, and on evaporation **does not give any crystals whatever. If the green solution be kept**, however, for several weeks at the ordinary temperature, it will deposit **violet crystals** of chrome alum. The green solution, when evaporated, gives a non-crystalline mass. The transition of the green modification into the violet is accompanied by a decrease in volume (Lecoq de Boisbaudran, Favre).

Not chrome alum alone, but all the chromic salts, give **green** and **violet modifications**. The green chromic salts, obtained by heating solutions of the violet salts, give violet solutions if kept for a long time. Chromic oxide, like alumina, is able to give both acid and basic salts. It is supposed that the difference between the green and violet salts is due to this fact. This opinion of Krüger is based on the fact that alcohol throws out from the green solution a salt which contains less sulphuric acid than the normal violet salt. On the other hand, Löwel showed that all the acid cannot be separated from the green chromic salts by suitable reagents, as easily as it can be from the same solution of the violet salts; thus barium salts do not precipitate all the sulphuric acid from solutions of the green salts. Recoura (1890–1896) showed that there are two kinds of green salts. If a solution of the crystalline violet chromium sulphate, $Cr_2(SO_4)_3,8H_2O$, is boiled, it gives one variety, while if the crystals of the sulphate are cautiously heated they lose $10H_2O$, and give another variety, which forms the same green solution as the first. Recoura found that one equivalent of sulphuric acid is lost per 2 molecules of salt in the formation of the first variety, and that only one equivalent of sulphuric acid out of the five it contains reacts with $BaCl_2$, precipitating $BaSO_4$. He considers this first variety to contain a peculiar complex salt, $(Cr_4S_4O_{17})SO_4$, corresponding to a hydrate, and in general to $(Cr_4S_4O_{17})X_2$, or with the addition of water to $[Cr_4(SO_4)_4(OH)_2]X_2$. Hence from its composition, $4CrX_3$, this is a basic chromic salt. The other variety, having the composition of the normal neutral salt, $Cr_2(SO_4)_3$, gives no precipitate at all with a solution of BaX_2, and is able to combine with yet another molecule of sulphuric acid or its salts, and the resulting salts are not precipitated by $BaCl_2$, but, after the addition of sulphuric acid, with CuX_2 give a precipitate of a copper salt of chromo-sulphuric acid, $(Cr_2S_4O_{16})Cu$. Recoura obtained compounds with 2, 3, 4, and $5H_2SO_4$, but they all give the above precipitate with cupric salts, and evolve more heat with bases than the sulphuric acid they contain. Wyrouboff (1902) applied to the abnormal (not directly reacting with $BaCl_2$) sulphate compounds of chromic oxide the view that their 'complex' properties are due to the fact that some of the hydroxyls in $Cr_2(OH)_6$ acquire the property of alcoholic hydroxyls; however, as no difference is to be seen between the hydroxyl in Na(OH) and that in any alcohol, for instance, $CH_3(OH)$, the difference in the mode of reaction of NaX and CH_3X can only be ascribed to the difference between Na and CH_3, or in the manner in which they are united with (OH), and the cause of the peculiar reactions and of the isomerism of the violet and green compounds of chromic oxide cannot yet be considered as satisfactorily explained. And as similar 'complex' organic compounds (alcohols and others) are always composed of many elements, a portion of which are non-atomic, it appears to me that the explanation of this case chloride of chromium, Cr_2Cl_6, and in the employment of the hydrate as a mordant in dyeing, &c.[8]

---

should be sought in the same light as for the organic compounds (Vol. I., pp. 391 *et seq.*). For my part I think that here, as with the organic compounds, we require a number of well-investigated experimental data before looking for any explanation, and that as the chromic salts cannot be said to be thoroughly investigated (for instance, their molecular weights are unknown, and also their behaviour with respect to ammonia, the chloranhydrides and fluorides, &c.), this class of compounds ought to be regarded as a matter deserving detailed research.

Potassium and **sodium hydroxides** give a **precipitate** of the hydroxide with chromic salts, CrX_3. The violet and green salts give a **hydroxide soluble in an excess of the reagent**; but the hydroxide is held in solution by very feeble affinities, so that it is partially separated by heat and dilution with water, and completely so on boiling. In an alkaline solution, chromic hydroxide is easily converted into chromic acid by the action of lead dioxide, chlorine, and other oxidising agents. If the chromic oxide occurs together with such oxides as magnesia, or zinc oxide, then on precipitation it separates out from its solution in combination with these oxides, forming, for example, ZnO,Cr_2O_3 (Viard). When fused with borax, chromic salts give a green glass. The same coloration is communicated to ordinary glass by the presence of traces of chromic oxide. A chrome glass containing a large amount of chromic oxide may be ground up and used as a green pigment. Among the hydrates of oxide of chromium **Guignet's green** forms one of the green pigments which have been substituted for the poisonous arsenical copper pigments (Schweinfurt's green). Guignet's green has an extremely bright-green colour, and is distinguished for its great stability, not only under the action of light but also towards reagents; thus, it is not altered by alkaline solutions, and even nitric acid does not act on it. This pigment remains unchanged up to a temperature of 250°; it contains $Cr_2O_32H_2O$, and generally a small amount of alkali. It is prepared by fusing 3 parts of boric acid with 1 part of potassium dichromate; oxygen is disengaged, and a green glass, containing a mixture of the borates of chromium and potassium, is obtained. When cool this glass is ground up and treated with water, which extracts the boric acid and alkali and leaves the above-named chromic hydroxide behind. This hydroxide only parts with its water at a red heat, leaving the anhydrous oxide.

The chromic hydroxides lose their water by ignition, and in so doing become spontaneously incandescent, like the ordinary ferric hydroxide (Chap. XXII.). It is not known, however, whether all the modifications of chromic oxide show this phenomenon. The anhydrous **chromic oxide**, Cr_2O_3, is exceedingly difficultly soluble in acids, if it has passed through the above recalescence. But if it has parted with its water, or the greater part of it, and not yet undergone this self-induced incandescence (has not lost a portion of its energy), it is soluble in acids. It is not reduced by hydrogen. The chromates of mercury and ammonium give a very convenient method for its preparation, because when ignited they leave chromic oxide behind. In the first instance, $2Hg_2CrO_4 = Cr_2O_3 + O_5 + 4Hg$, and in the second $(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$. The second reaction is very energetic, and the mass of salt burns spontaneously if the temperature is sufficiently high. A mixture of potassium sulphate and chromic oxide is formed by heating potassium dichromate with an equal weight of sulphur: $K_2Cr_2O_7 + S = K_2SO_4 + Cr_2O_3$. The sulphate is easily extracted by water, and there remains a bright-green residue of the oxide, the colour of which is more brilliant the lower the temperature of the decomposition. The oxide thus obtained is used as a green pigment for china and enamel. The crystalline anhydrous chromic oxide has a specific gravity of 5·2–5·6, and is almost black and gives a green powder. The crystals are hard enough to scratch glass, and have a metallic lustre. The crystalline form of chromic oxide is identical with that of the oxide of iron and alumina, with which it is isomorphous.

[8] The most important of the compounds corresponding with chromic oxide is **chromic chloride**, Cr_2Cl_6, which is known in an anhydrous and a hydrated form. The former is insoluble in water, the latter easily dissolves, and on evaporation its solution leaves a

Chromic oxide, Cr_2O_3, found rarely, and in small quantities, in chrome ochre, is formed by the oxidation of chromium and its lower

hygroscopic mass, which is very unstable and readily evolves hydrochloric acid when heated with water. The anhydrous form is of a violet colour, and according to Wöhler is formed by heating an intimate mixture of the anhydrous chromic oxide with carbon and organic matter in a stream of dry chlorine; a slightly volatile sublimate of chromic chloride, $CrCl_3$, is thus formed. This substance forms **violet tabular crystals**, greasy to the touch and insoluble in water; but if they are powdered and boiled in water for a long time they pass into a **green solution**. Strong sulphuric acid does not act on the anhydrous salt, or only acts with exceeding slowness, like water. Even aqua regia and other acids do not act on the crystals, and alkalies only show a very feeble action. The specific gravity of the crystals is 2·99. When fused with sodium carbonate and nitre they give sodium chloride and potassium chromate, and when ignited in air they form green chromic oxide and evolve chlorine. On ignition in a stream of ammonia, chromic chloride forms sal-ammoniac and chromium nitride, CrN (analogous to the nitrides BN,AlN). Mosberg and Peligot showed that when chromic chloride is ignited in hydrogen, it parts with one-third of its chlorine, forming chromous chloride, $CrCl_3$—that is, there is formed from a compound corresponding with chromic oxide, Cr_2O_3, a compound answering to the **suboxide**, chromous oxide, CrO—just as hydrogen converts ferric chloride into ferrous chloride with the aid of heat. **Chromous chloride**, $CrCl_2$, forms colourless crystals readily soluble in water, which, in dissolving, evolve a considerable amount of heat and form a blue liquid, capable of absorbing oxygen from the air with great facility, being converted thereby into a chromic compound.

The blue solution of chromous chloride may also be obtained by the action of metallic zinc on the green solution of the hydrated chromic chloride. The zinc must be employed in large excess, but if the solution remains for a long time in contact with the zinc the whole of the chromium is converted into chromic oxychloride. Other chromic salts are also reduced by zinc into **chromous salts**, CrX_2. The reducing power of these salts is very great. From cupric salts they separate cuprous salts, from stannous salts they precipitate metallic tin, and they reduce mercuric salts into mercurous and ferric into ferrous salts. Moreover, they absorb oxygen from the air directly. With potassium chromate they give a brown precipitate of chromium dioxide or of chromic oxide, according to the relative amounts of the substances taken: $CrO_3 + CrO = 2CrO_2$ or $CrO_3 + 3CrO = 2Cr_2O_3$. Aqueous ammonia gives a blue precipitate, and in the presence of ammoniacal salts a blue liquid is obtained which turns red in the air owing to oxidation. This is accompanied by the formation of compounds analogous to those given by cobalt (Chap. XXII.). A mixture of chromous chloride solution with a hot saturated solution of sodium acetate, $C_2H_3NaO_2$, gives, on cooling, transparent red crystals of chromous acetate, $C_4H_6CrO_4,H_2O$. This salt is also a powerful reducing agent, but may be kept for a long time in a vessel full of carbonic anhydride.

The insoluble anhydrous *chromic chloride* $CrCl_3$ very easily *passes into solution* in the presence of a trace (0·004) of *chromous chloride*, $CrCl_2$. This remarkable phenomenon was observed by Peligot and explained by Löwel in the following manner: chromous chloride, as a lower stage of oxidation, is capable of absorbing both oxygen and chlorine, combining with various substances. It is able to decompose many chlorides by taking up chlorine from them; thus it precipitates mercurous chloride from a solution of mercuric chloride, and in so doing passes into chromic chloride: $2CrCl_2 + 2HgCl_2 = Cr_2Cl_6 + 2HgCl$. Let us suppose that the same phenomenon takes place when the $CrCl_3$ is mixed with a solution of $CrCl_2$. The latter will then take up a portion of the chlorine of the former, and pass into a soluble hydrate of $CrCl_3$ (hydrochloride of oxide of chromium), and the $CrCl_3$ will pass into $CrCl_2$. The chromous chloride re-formed in this manner will then act on a fresh quantity of the chromic chloride, and so on. This view is confirmed by the fact that other chlorides, capable of absorbing chlorine like chromous chloride, also induce the solution of the insoluble chromic chloride—for example, ferrous chloride, $FeCl_2$, and cuprous chloride. The solution of chromic oxides, by the reduction of chromates (for example, of ammonium or mercuric chromate) and by the decomposition (splitting up) of the saline

chloride in water obtained by these methods is perfectly identical with that formed by dissolving chromic hydroxide in hydrochloric acid. On evaporating the **green solution** obtained in this manner, it gives a green mass, containing water. On further heating it leaves a soluble chromic oxychloride, and when ignited it first forms an insoluble oxychloride and then chromic oxide; but no anhydrous chromic chloride, Cr_2Cl_6, is formed by heating the aqueous solution of chromic chloride. At 100° the composition of the green hydrate is $Cr_2Cl_6,9H_2O$, and on evaporation at the ordinary temperature over H_2SO_4 crystals are obtained with 12 equivalents of water; the red mass obtained at 120° has the composition $Cr_2O_3,4Cr_2Cl_6,24H_2O$. The greater portion of it is soluble in water, like the mass which is formed at 150°. The latter consists of $Cr_2O_3,2Cr_2Cl_6,9H_2O = 3(Cr_2OCl_4,3H_2O)$—that is, it presents the same composition as chromic chloride in which one atom of oxygen replaces two of chlorine. And if the hydrate of chromic chloride be regarded as $Cr_2O_3,6HCl$, the substance which is obtained should be regarded as $Cr_2O_3,4HCl$ combined with water, H_2O. The addition of alkalies—for example, baryta—to a solution of chromic chloride immediately produces a precipitate, which, however, re-dissolves on shaking, owing to the formation of one of the oxychlorides just mentioned, which may be regarded as **basic salts**. Thus we may represent the product of the change produced in chromic chloride under the influence of water and heat by the following formulæ: first $Cr_2O_3,6HCl$ or $Cr_2Cl_6,3H_2O$ is formed, then $Cr_2O_3,4HCl,H_2O$ or $Cr_2OCl_4,3H_2O$, and lastly $Cr_2O_3,2HCl,2H_2O$ or $Cr_2O_2Cl_2,3H_2O$. In all three cases there are 2 equivalents of chromium to at least 3 equivalents of water. These compounds are intermediate between chromic hydroxide and chloride.

It is very important, in this connection, to notice two facts: (1) That the whole of the chlorine in the above compounds is not precipitated from their solutions by silver nitrate; thus, the normal salt of the composition $Cr_2Cl_6,9H_2O$ only gives up two-thirds of its chlorine. Therefore Peligot supposes that the normal salt contains the oxychloride combined with hydrochloric acid: $Cr_2Cl_6 + 2H_2O = Cr_2O_2Cl_2,4HCl$, and that the chlorine held as hydrochloric acid reacts with the silver, whilst that held in the oxychloride does not enter into reaction, just as we observe a very feebly developed faculty for reaction in the anhydrous chromic chloride. (2) If the green aqueous solution of $CrCl_3$ is left to stand for some time, it ultimately turns violet; in this form the whole of the chlorine is precipitated by $AgNO_3$, whilst boiling reconverts it into the green variety. Löwel obtained the violet solution of hydrochloride of chromic oxide by decomposing the violet chromic sulphate with barium chloride. But if the violet solution be boiled, and so converted into the green modification, silver nitrate will then only precipitate a portion of the chlorine.

Recoura (1890–1893) obtained a crystallohydrate of violet chromium sulphate, $Cr_2(SO_4)_3$, with 18 or 15 H_2O. By boiling a solution of this crystallohydrate, he converted it into the green salt, which, when treated with alkalies, gave a precipitate of $Cr_2O_3,2H_2O$, soluble in $2H_2SO_4$ (and not 3), and only forming the basic salt, $Cr_2(OH)_2(SO_4)_2$. He therefore concludes that the green salts are basic salts. The cryoscopic determination made by A. Speransky (1892) and by Marchetti (1892) give a greater 'depression' for the violet than for the green salts, indicating a greater molecular weight for the latter.

Piccini's researches (1894) throw an important light upon the peculiarities of the green $CrCl_3$; he showed (1) that AgF (in contradistinction to the other salts of silver) precipitates all the chlorine from an aqueous solution of the green variety; (2) that solutions of green $CrCl_3,6H_2O$ in ethyl alcohol and acetone precipitate all their chlorine when mixed with a similar solution of $AgNO_3$; (3) that the rise of the boiling-point of the green ethyl alcohol and acetone solutions of $CrCl_3,6H_2O$ (Chap. VII., note 27a) shows that *i* in this case (as in the aqueous solutions of $MgSO_4$ and $HgCl_2$) is nearly equal to 1, that is, that they are like solutions of non-conductors; (4) that a solution of green $CrCl_3$ in methyl alcohol at first precipitates about $\frac{1}{3}$ of its chlorine (an aqueous solution about $\frac{2}{3}$) when treated with $AgNO_3$, but after a time the whole of the chlorine is precipicompounds of the oxide itself, CrX_3 or Cr_2X_6, like alumina, which it resembles in forming a feeble base, readily forming double and basic salts, besides neutral CrX_3. In this respect it is particularly noticeable that the chromic salts can be either violet or green, even when of exactly the same composition, so that the application of heat or other change of conditions converts violet solutions into green, which again gradually become violet at the ordinary temperature. The difference is not limited to colour, but is also seen in the physical and chemical properties. The salts of the violet variety usually crystallise with ease, while the green salts often do not. The former immediately enter into double saline decompositions in which the whole of their haloid participates, while only a portion enters into reaction in the case of the green salts (see notes 7 and 8). Although this remarkable instance of isomerism has formed and is forming the object of research, it still remains unexplained in many relations, and in its essential points recalls the case of phosphoric acid.

Although chromic oxide is not acted on by hydrogen at a high temperature, it is reduced with comparative ease in the form of solutions

---

tated; and (5) that an aqueous solution of the green variety gradually passes into the violet, while a methyl alcohol solution preserves its green colour, both of itself and also after the whole of the chlorine has been precipitated by $AgNO_3$. If, however, in an aqueous or methyl alcoholic solution only a portion of the chlorine is precipitated, the solution gradually turns violet.

The green modification of chromic chloride does not give double salts with the metallic chlorides, whilst the violet variety forms compounds, $Cr_2Cl_6,2RCl$ (where R is an alkali metal). As the result of all the existing researches on the green and violet chromic salts, it appears to me most probable that their difference is determined by the feeble basic character of chromic oxide, by its faculty of giving basic salts, and by the colloidal properties of its hydroxide (these three properties are mutually connected), and, moreover, it seems to me that the relation between the green and violet salts of chromic oxide answers best to that between the different hydrates of phosphoric acid (Chap. XIX.) or to the relation of the purpureo- to the luteo-cobaltic salts (Chap. XXII., note 35).

But this leads to problems of another kind, more complex and difficult to understand, owing to the insufficiency of the existing chemical data, and especially on account of the incapacity evinced by the chlorine in salts containing it for reacting with silver salts. This recalls the long known case of the double cyanides such as ferricyanide of potassium, the cyanogen of which does not exhibit any of those reactions (instantaneous) of double decomposition proper to the ordinary cyanides. Although they have been assumed to contain complex radicles, still it is simpler to recognise in them the influence of the association of an aggregation of elements (of multiple and variable valency) which directs the reaction in a different course. The other side of the question is still more complicated. Here we have polymerides, colloidal forms, and cases of isomerism (see Chap. XXII., Fe_2O_3). It seems to me that the recognition of complex radicles (or, what is essentially the same, of special ions) as an explanation of such phenomena does not answer to the true principles of science, for it only gives, I think, a new means of expressing facts, and not of explaining them, and therefore it appears to me that the essence of those differences which are found in the green varieties of the chromic salts is not yet quite clear, and that these substances offer a wide field, like many other branches of our science, for future research.

of its salts, CrX_3. Such reducing agents as Zn and H_2SO_4 convert them into chromous salts, CrX_2; while others, such as sodium amalgam, even reduce it to metallic chromium. The salts of the suboxide, CrX_2, form blue solutions and themselves act as powerful reducing agents, and even absorb free oxygen.

Metallic chromium was obtained by Deville (probably containing carbon) by reducing chromic oxide with carbon at a temperature near the melting-point of platinum. Chromium (sp. gr. 5·9) has a steel-grey colour, and is very hard, takes a good polish, and dissolves in hydrochloric acid, but cold dilute sulphuric and nitric acids have no action upon it. Bunsen obtained metallic chromium by decomposing a solution of chromic chloride, Cr_2Cl_6, by a galvanic current, as scales of a grey colour (sp. gr. 7·3). Wöhler obtained crystalline chromium by igniting a mixture of the anhydrous chromic chloride (Cr_2Cl_6; note 7a) with finely divided zinc, and sodium and potassium chlorides, at the boiling-point of zinc. When the resultant mass has cooled, the zinc may be dissolved in dilute nitric acid, and grey crystalline chromium (sp. gr. 6·81) is left behind. Frémy also prepared crystalline chromium by the action of the vapour of sodium on anhydrous chromic chloride in a stream of hydrogen. The crystals of metallic chromium were grey cubes having a considerable hardness and withstanding the action of acids. Gladzel (1890) obtained a crystalline powder of Cr by heating the double chloride $KCrCl_4$ with magnesium. Its sp. gr. was 6·7, and it dissolved readily in acids with the evolution of hydrogen. This seems to indicate a discrepancy between the results of different investigators, which has only been recently explained. Moissan (1893) heated chromic oxide with carbon in the electric furnace, and at first obtained chromium carbide (two carbides are known, Cr_2C and Cr_3C_2, both extremely hard), and then, after the addition of a fresh amount of Cr_2O_3, *fused* metallic chromium of a white colour, malleable and capable of taking a fine polish. Goldschmidt (1900) proposed to obtain fused chromium by heating oxide of chromium with aluminium powder. Metallic chromium (and its alloy with iron) is manufactured on a large scale for steel works, as it endows steel with great hardness. The sp. gr. of the purest chromium is about 6·8. It fuses at 1,800°. It acts on acids with greater energy the more impurities (apparently Si and Fe) it contains; it evolves hydrogen with HCl, forming $CrCl_2$; but an acid solution of this chromous compound (blue) is easily converted into the chromic compound, $CrCl_3$, with the evolution of hydrogen by contact action (platinum black, &c.) (Doring, 1902). However, metallic chromium in the presence of acids at the ordinary temperature or by superficial oxidation as an anode, &c., easily becomes passive and ceases to act on acids; but if this passive chromium be heated with an acid it again becomes active (Hittorf, 1899), and this accounts for the discrepancy in the first statements respecting the action of acids upon metallic chromium.

Chromium is employed as an ingredient in steel, for 3 per cent. of Cr, and one and a half of C, render steel exceedingly hard. An alloy of iron and chromium is sometimes prepared for this purpose by directly reducing chrome iron ore in the blast furnace.

The two analogues of chromium, **molybdenum** and **tungsten** (or wolfram), are of still rarer occurrence in nature, and form acid oxides, RO_3, which are still less energetic than CrO_3.[8a] Tungsten occurs in the some-

---

[8a] The atomic compositions of the tungsten and molybdenum compounds are taken as being identical with that of the compounds of sulphur and chromium, because (1) both these metals give two oxides in which the amounts of oxygen per given amount of metal stand in the ratio 2 : 3; (2) the higher oxide is of the latter kind, and, like chromic and sulphuric anhydrides, it has an acid character; (3) certain of the molybdates are isomorphous with the sulphates; (4) the specific heat of tungsten is 0·0334, consequently the product of the atomic weight and specific heat is 6·15, like that of the other elements —it is the same with molybdenum, 96·0 × 0·0722 = 6·9; (5) tungsten forms with chlorine not only compounds, WCl_6, WCl_5, and $WOCl_4$, but also WO_2Cl_2, a volatile substance and the analogue of chromyl chloride, CrO_2Cl_2, and of sulphuryl chloride, SO_2Cl_2. Molybdenum gives the chlorine compounds, $MoCl_2$, $MoCl_3$(?), $MoCl_4$ (fuses at 194°, boils at 268°; according to Debray it has the composition $MoCl_5$), $MoOCl_4$, MoO_2Cl_2, and $MoO_2(OH)Cl$. The existence of tungsten hexachloride, WCl_6, is an excellent proof of the fact that the type SX_6 appears in the analogues of sulphur as in SO_3; (6) the vapour density accurately determined for the chlorine compounds, $MoCl_4$, WCl_6, WCl_5, $WOCl_4$ (Roscoe), leaves no doubt as to the molecular composition of the compounds of tungsten and molybdenum, for the observed and calculated results entirely agree.

Tungsten is sometimes called 'scheele' in honour of Scheele, who discovered it in 1781, and molybdenum in 1778. Tungsten is also known as 'wolfram'; the former name was the name given to it by Scheele, because he extracted it from the mineral then known as tungsten and now called scheelite, $CaWO_4$. The researches of Roscoe, Blomstrand, and others have subsequently thrown considerable light on the whole history of the compounds of molybdenum and tungsten.

The ammonium salts of tungstic and molybdic acids, when ignited, leave the anhydrides, which resemble each other in many respects. **Tungstic anhydride**, WO_3, is a yellowish substance, which only fuses at a strong heat, and has a sp. gr. of 6·8. It is insoluble both in water and acid, but solutions of the alkalies, and even of the alkali carbonates, dissolve it, especially when heated, forming alkaline salts. **Molybdic anhydride**, MoO_3, is obtained by igniting the acid (hydrate) or its ammonium salt, and forms a white mass which fuses at a red heat, and solidifies to a yellow crystalline mass of sp. gr. 4·4; whilst on further heating this anhydride **sublimes** in pearly scales—this enables it to be obtained in a tolerably pure state. Water dissolves it in small quantities—1 part requires 600 parts of water for its solution. The hydrates of molybdic anhydride are *soluble also in acids* (a hydrate, H_2MoO_4, is obtained from the nitric acid solution of the ammonium salt), which forms one of their distinctions from the tungstic acids. But after ignition, molybdic anhydride is insoluble in acids, like tungstic anhydride; alkalies dissolve this anhydride forming molybdates. Potassium bitartrate dissolves the anhydride with the aid of heat. None of the acids yet considered by us form so many different salts with one and the same base (alkali) as do molybdic and tungstic acids. The composition of these salts, and their properties also, vary considerably. The most important discovery in this respect was made by Marguerite and Laurent, who showed that the salts which contain a large proportion of tungstic acid are easily soluble in water, what rare minerals, scheelite, $CaWO_4$, and wolfram, the latter being an isomorphous mixture of the normal tungstates of iron and manganese,

and ascribed this property to the fact that tungstic acid may be obtained **in several states**. The common tungstates, obtained with an excess of alkali, have an alkaline reaction, and on the addition of sulphuric or hydrochloric acid deposit first an acid salt and then a hydrate of tungstic acid, which is insoluble both in water and acids; but if, instead of sulphuric or hydrochloric acid, we add acetic or phosphoric acid, or if the tungstate be saturated with a fresh quantity of tungstic acid, which may be done by boiling the solution of the alkali salt with the precipitated tungstic acid, a solution will be obtained which, on the addition of sulphuric or a similar acid, does not give a precipitate of tungstic acid at the ordinary or at higher temperatures. The solution is then considered to contain salts of a peculiar acid which Laurent, Riche, and others called **metatungstic acid.** Those salts which with acids immediately give the insoluble tungstic acid have the composition R_2WO_4, $RHWO_4$, whilst those which give the soluble metatungstic acid contain a far greater proportion of the acid elements. Scheibler obtained the (soluble) metatungstic acid itself by treating the soluble barium (meta-) tetratungstate, $BaO,4WO_3$, with sulphuric acid. Subsequent research showed the existence of a similar phenomenon for molybdic acid. There is no doubt that this is a case of colloidal modifications and of differences like those of the phosphoric acids.

The tungstates and molybdates have been investigated by Marguerite, Laurent, Marignac, Riche, Scheibler, Struve and Svanberg, De la Fontaine, and others. For a given amount of base the salts contain one to eight equivalents of molybdic or tungstic anhydride; i.e., if the base have the composition RO, the highest proportion of base will be contained by the salts of the composition RO,WO_3 or RO,MoO_3—that is, by those salts which correspond with the normal acids H_2WO_4 and H_2MoO_4 of the same nature as sulphuric acid; but there also exist salts of the composition $RO,2WO_3$, $RO,3WO_3$ . . . $RO,8WO_3$. The water contained in the composition of the poly-acid salts is often not taken into account. The properties of the salts holding different proportions of acid oxide vary considerably, but one salt may be converted into another with great facility by the addition of acid or base, and the greater the proportion of the elements of the acid in a salt, the more stable, within a certain limit, is its solution and the salt itself. Muslins, &c., are sometimes treated with a solution of sodium tungstate to render them non-inflammable, for instance, for use on the stage.

The most common **ammonium molybdate** has the composition $(NH_4HO)_6,H_2O,7MoO_3$ (or, according to Marignac and others, NH_4HMoO_4), and is prepared by evaporating an ammoniacal solution of molybdic acid. It is used in the laboratory for precipitating phosphoric acid, and is purified for this purpose by mixing its solution with a small quantity of magnesium nitrate in order to precipitate any phosphoric acid present, filtering, and then adding nitric acid and evaporating to dryness. A pure ammonium molybdate free from phosphoric acid may then be extracted from the residue.

Phosphoric acid forms insoluble compounds with the oxides of uranium, iron, tin, bismuth, &c., having feeble basic and even acid properties. This depends perhaps on the fact that the atoms of hydrogen in phosphoric acid are very varied in character, as we saw above. Those atoms of hydrogen which are replaced with difficulty by ammonium, sodium, &c., are probably easily replaced by feebly energetic acid groups; that is, the formation of particular complex substances may be expected to take place at the expense of these hydrogen atoms of phosphoric acid and of certain feeble metallic acids; and these substances will still be acids, because the hydrogen of the phosphoric acids and metallic acids, which is easily replaced by metals, is not removed by their mutual combination, but remains in the resultant compound. Such a conclusion is verified in the **phosphomolybdic acids** obtained (1888) by Debray. If a solution of ammonium molybdate be acidified, and a small amount of a solution (it may be acid) containing orthophosphoric acid or its salts be added to it (so that there are

$(MnFe)WO_4$. Molybdenum is most frequently met with as molybdenite, MoS_2, which presents a certain resemblance to graphite in its physical

---

at least 40 parts of molybdic acid present to 1 part of phosphoric acid), then, after a period of twenty-four hours, the whole of the phosphoric acid will be separated as a yellow precipitate, containing, however, not more than 3 to 4 per cent. of phosphoric anhydride, about 3 per cent. of ammonia, about 90 per cent. of molybdic anhydride, and about 4 per cent. of water. The formation of this precipitate is so distinct and so complete that this method is employed for the detection and separation of the smallest quantities of phosphoric acid. Phosphoric acid was found by this means to be present in the majority of rocks. The precipitate is soluble in ammonia and its salts, in alkalies and phosphates, but is perfectly insoluble in nitric, sulphuric, and hydrochloric acids in the presence of ammonium molybdate. The composition of the precipitate appears to vary under the conditions of its precipitation, but its nature became clear when the acid corresponding with it was obtained. If the above-described yellow precipitate is boiled in aqua regia, the ammonia is destroyed, and an acid is obtained in solution, which when evaporated in the air crystallises out in yellow oblique prisms of approximately the composition, $P_2O_5,20MoO_3,26H_2O$ (generally considered to consist of $H_3PO_4,12H_2MoO_4 = P_2O_5,24MoO_3,27H_2O$; most probably the amount of MoO_3 is variable). Such an unusual proportion of component parts is explained by the above-mentioned considerations. We saw above that molybdic acid readily gives salts $R_2O,nMoO_3,mH_2O$, which we may imagine to correspond to a hydrate $MoO_2(HO)_2,nMoO_3,mH_2O$. And we may suppose that such a hydrate reacts on orthophosphoric acid, forming water and compounds of the composition $MoO_2(HPO_4),nMoO_3,mH_2O$ or $MoO_2(H_2PO_4)_2,nMoO_3,mH_2O$; this is actually the composition of phosphomolybdic acid. Probably it contains a portion of the hydrogen, replaceable by metals, of both the acids H_3PO_4 and of H_2MoO_4. The crystalline acid above is probably $H_3MoPO_7,9MoO_3,12H_2O$. This acid is really tribasic, because its aqueous solution precipitates salts of potassium, ammonium, rubidium (but not lithium and sodium) *from acid solutions*, and gives a *yellow* precipitate of the composition $R_3MoPO_7,9MoO_3,3H_2O$, where $R = NH_4$, or K. Besides these, salts of another composition may be obtained, as would be expected from the preceding. These salts are only stable in acid solutions (which is naturally due to their containing an excess of acid oxides), whilst under the action of alkalies they give *colourless* phosphomolybdates of the composition $R_3MoPO_7,MoO_2,3H_2O$. The corresponding salts of potassium, silver, and ammonium, are easily soluble in water and crystalline.

Phosphomolybdic acid is an example of the **complex inorganic acids** first obtained by Marignac and afterwards generalised and studied in detail by Gibbs. We shall afterwards meet with several examples of such acids, and we will now call attention to the fact that they are usually formed by weak polybasic acids (boric, silicic, molybdic, &c.), and in certain respects resemble the cobaltic and similar complex compounds with which we shall become acquainted in the following chapter. As an example, we may mention certain complex compounds containing molybdic and tungstic acids. The action of ammonium molybdate upon a dilute solution of purpureo-cobaltic salts (see Chap. XXII.) acidulated with acetic acid gives a salt which, after drying at 100° has the composition $Co_2O_3,10NH_3,7MoO_3,3H_2O$. After ignition this salt leaves a residue having the composition $2CoO,7MoO_3$. An analogous compound is also obtained for tungstic acid, having the composition $Co_2O_3,10NH_3,10WO_3,9H_2O$. In this case, after ignition there remains a salt of the composition $CoO,5WO_3$ (Carnot, 1889). Professor Kurnakoff (1889), by treating a solution of potassium and sodium molybdates containing suboxide of cobalt, CoO, with bromine, obtained salts of the oxide Co_2O_3 having the composition: $3K_2O,Co_2O_3,12MoO_3,20H_2O$ (light-green) and $3K_2O,Co_2O_3,10MoO_3,10H_2O$ (dark-green). Péchard (1893) obtained salts of the four complex phosphotungstic acids by evaporating equivalent mixtures of solutions of phosphoric and metatungstic acids: phosphotrimetatungstic acid, $P_2O_5,12WO_3,48H_2O$, phosphotetrametatungstic acid, $P_2O_5,16WO_3,69H_2O$, phosphopentametatungstic acid, $P_2O_5,20WO_3,H_2O$, &c. Kehrmann (1892) considers the possibility of obtaining an unlimited number of such salts to properties and softness. It also occurs, but much more rarely, as a yellow lead ore, $PbMoO_4$. In both these forms molybdenum occurs in

be a general characteristic of such compounds. Mahom and Friedheim (1892) obtained compounds of similar complexity for molybdic and arsenic acids.

Normal sodium tungstate, Na_2WO_4, is obtained by heating a strong solution of sodium carbonate with tungstic acid to a temperature of 80°; if the solution is filtered hot, it crystallises in rhombic tabular crystals, having the composition $Na_2WO_4,2H_2O$, which remain unchanged in the air and are easily soluble in water. When this salt is fused with a fresh quantity of tungstic acid, it gives a ditungstate, which is soluble in water and separates from its solution in crystals containing water. The same salt is obtained by carefully adding hydrochloric acid to the solution of the normal salt so long as a precipitate does not appear, and the liquid still has an alkaline reaction. This salt has the composition (at 100°) $Na_6W_8O_{24},16H_2O$—that is, it corresponds with the similar salt of molybdic acid.

If this salt is heated to a red heat in a stream of hydrogen, it loses a portion of its oxygen, acquires a metallic lustre, and turns a golden-yellow colour, and, after being treated with water, alkali, and acid, leaves golden-yellow leaflets and cubes which are very like gold. This very remarkable substance, discovered by Wöhler, has, according to Malaguti's analysis, the composition $Na_2W_3O_9$; that is, it consists, as it were, of a double tungstate of tungsten oxide, WO_2, and of sodium, Na_2WO_4,WO_2WO_3. With potassium, only one compound is formed (according to Knorre and Schäfer, 1902), of the composition $K_2W_4O_{12}$, whilst sodium gives compounds of varying composition, but all possessing the properties of *tungsten bronzes*, the most remarkable of these being the power of conducting a current like metals. The decomposition of the fused sodium salt is best effected by finely divided tin. This substance has a sp. gr. 6·6; it conducts electricity like metals, and like them has a metallic lustre. When brought into contact with zinc and sulphuric acid it disengages hydrogen, and becomes covered with a coating of copper in a solution of copper sulphate in the presence of zinc—that is, notwithstanding its complex composition it presents to a certain extent the appearance and reactions of the metals. It is not acted on by aqua regia or alkaline solutions, but is oxidised when ignited in air.

The ditungstate mentioned above, deprived of water (having undergone a modification similar to that of metaphosphoric acid), after being treated with water, leaves an anhydrous, sparingly soluble tetratungstate, $Na_2WO_4,3WO_3$, which, when heated at 120° in a closed tube with water, passes into an easily soluble metatungstate. It may therefore be said that the metatungstates are hydrated compounds. On boiling solutions of the above-mentioned salts of sodium with the yellow hydrate of tungstic acid, they give a solution of metatungstate, which is the hydrated tetratungstate. Its crystals have the composition $Na_2W_4O_{13},10H_2O$. After the hydrate of tungstic acid has stood a long time in contact with a solution of sodium tungstate, it gives a solution which is not precipitated by hydrochloric acid; this must be filtered and evaporated over sulphuric acid in a desiccator (it is decomposed by boiling). It first forms a very dense solution (aluminium floats in it) of sp. gr. 3·0, and octahedral crystals of **sodium metatungstate**, $Na_2W_4O_{13},10H_2O$, of sp. gr. 3·85, then separate. It effloresces and loses water, and at 100° only two out of the ten equivalents of water remain, but the properties of the salt remain unaltered. If the salt is deprived of water by further heating, it becomes insoluble. At the ordinary temperature one part of water dissolves ten parts of the metatungstate. The other metatungstates are easily obtained from this salt. Thus a strong and hot solution, mixed with a similar one of barium chloride, gives, on cooling, crystals of **barium metatungstate**, $BaW_4O_{13},9H_2O$. These crystals are dissolved without change in water containing hydrochloric acid, and also in hot water, but they are partially decomposed by cold water, with the formation of a solution of metatungstic acid and of the normal barium salt, $BaWO_4$.

It is noticeable that a mixture of a solution of tungstic acid with a solution of silicic acid does not coagulate when heated, although the silicic acid alone would do so; this is the primary rocks, in granites, gneiss, &c., and in iron and copper ores in Saxony, Sweden, and Finland. Tungsten ores are sometimes met

due to the formation of a **silicotungstic acid**, discovered by Marignac, which presents a fresh example of a complex acid. A solution of a tungstate dissolves gelatinous silica just as it does gelatinous tungstic acid, and when evaporated deposits a crystalline salt of silicotungstic acid. This solution is not precipitated either by acids (a clear analogy to the metatungstates) or by sulphuretted hydrogen, and corresponds with a series of salts. These salts contain one equivalent of silica and 8 equivalents of hydrogen or metals, in the same form as in salts, to 12 or 10 equivalents of tungstic anhydride; for example, the crystalline potassium salt has the composition $K_8W_{12}SiO_{42},14H_2O = 4K_2O,12WO_3,SiO_2,14H_2O$. Acid salts are also known in which half of the metal is replaced by hydrogen. Friedheim and Henderson obtained compounds of still greater complexity, for instance, crystals of a salt $(NH_4)_6SiV_2W_{10}O_{40},21H_2O$ and $(NH_4)_6SiV_2W_9O_{37},24H_2O$ (both contain in all 61 atoms of oxygen). The complexity of the composition of such complex acids (for example, of phosphomolybdic acid) involuntarily leads to the idea of polymerisation, which must be recognised for silica, lead oxide, and other compounds. This polymerisation, it seems to me, may be understood thus: a hydrate A (for example, tungstic acid) is capable of combining with a hydrate B (for example, silicic or phosphoric acid, with or without the disengagement of water), and by reason of this faculty it is capable of polymerisation—that is, A combines with A—combines with itself—just as aldehyde, C_2H_4O, or the cyanogen compounds are able to combine with hydrogen, oxygen, &c., and are liable to polymerisation. According to this view, the molecule of tungstic anhydride is probably much more complex than it is generally represented. Such a view also finds a certain confirmation in the researches made by Graham on the **colloidal** state of tungstic acid, because colloidal properties only appertain to compounds of a very complex composition. When sodium tungstate, mixed in dilute solution with an equivalent quantity of dilute hydrochloric acid, is placed in a dialyser, hydrochloric acid and sodium chloride pass through the membrane, and a solution of tungstic acid remains. The solution has a bitter, astringent taste, and does not yield gelatinous tungstic acid (hydrogel), either when heated or on the addition of acids or salts. It may also be evaporated to dryness; it then forms a vitreous mass of the **hydrosol of tungstic acid**, which adheres strongly to the walls of the vessel in which it has been evaporated, and is perfectly soluble in water. It does not even lose its solubility after having been heated to 200°. Its solution in a small quantity of water forms a gluey mass, just like gum arabic, which is one of the representatives of the hydrosols of colloidal substances. The solution, containing 5 per cent. of the anhydride, has a sp. gr. of 1·047; with 20 per cent., of 1·217; with 50 per cent., of 1·80; and with 80 per cent., of 8·24. The presence of a polymerised trioxide in the form of hydrate, H_2O,W_3O_9 or $H_2O,4WO_3$, must then be recognised in the solution: this is confirmed by Sabanéeff's cryoscopic determinations (1889). A similar stable solution of molybdic acid is obtained by the dialysis of a mixture of a strong solution of sodium molybdate with hydrochloric acid (the precipitate which is formed is re-dissolved). The addition of alkali to the solutions of the hydrosols of tungstic and molybdic acids immediately results in the re-formation of the ordinary tungstates and molybdates. There appears to be no doubt but that the same transformation is accomplished in the passage of the ordinary tungstates into the metatungstates as takes place in the passage of tungstic acid itself from an insoluble into a soluble state; but this may be even actually proved to be the case, because Scheibler obtained a solution of tungstic acid, before Graham, by decomposing barium metatungstate ($BaO,4WO_3,9H_2O$) with sulphuric acid. By treating this salt with sulphuric acid in the amount required for the precipitation of the baryta, Scheibler obtained a solution of metatungstic acid having specific gravities corresponding with those found by Graham.

Péchard found that as much heat is evolved by neutralising metatungstic acid as with sulphuric acid.

Questions connected with the metamorphoses or modifications of tungstic and with in considerable masses in the primary rocks of Bohemia and Saxony, and also in England, America, and the Urals. The preliminary treatment of the ore is very simple; for example, the sulphide, MoS_2, is roasted, and thus converted into sulphurous anhydride and molybdic anhydride, MoO_3, which is then dissolved in alkalies, generally in ammonia. The ammonium molybdate is then treated with acids, when the sparingly soluble molybdic acid is precipitated. Tungsten is treated in a different manner. Most frequently the finely ground ore is repeatedly boiled with hydrochloric and nitric acids, and the resultant solutions (of salts of manganese and iron) poured off, until the dark brown mass of ore disappears, whilst the tungstic acid remains, mixed with silica, as an insoluble residue; it is treated also with ammonia, and is thus converted into soluble ammonium tungstate, which passes into solution and yields tungstic acid when treated with acids. This hydrate is then ignited, and leaves tungstic anhydride. The general character of molybdic and tungstic anhydrides is analogous to that of chromic anhydride; they are anhydrides of a feebly acid character, which easily give polyacid salts and colloidal solutions, and, by reduction of the acids, the lower degrees of oxidation, Mo_2O_3, MoO_2, and WO_2.

Hydrogen reduces molybdic and tungstic anhydrides at a red heat. The metals are obtained, like Cr, by means of carbon in the electric furnace or with aluminium. Tungsten is used, like chromium, to give hardness, &c., to an alloy. **Both metals** are infusible, and under the action of heat form compounds with carbon and iron (the addition of tungsten to steel renders the latter ductile and hard).[9] Molybdenum forms a grey powder, which scarcely aggregates under the most powerful heat, and has a specific gravity of 9·0. It is not acted on by the air at the ordinary temperature, but when ignited it is first converted into a brown, and then into a blue oxide, and lastly into molybdic anhydride. Acids do not act on it—that is, it does not liberate hydrogen from them, not even from hydrochloric acid—but strong sulphuric acid, with the aid of heat, disengages sulphurous anhydride, forming a brown mass, containing a lower oxide of molybdenum. Alkalies in solution

---

molybdic acids, and the polymerisation and colloidal state of substances, as well as the formation of complex acids, belong to that class of problems the solution of which will do much towards attaining a true comprehension of the mechanism of a number of chemical reactions. I think, moreover, that questions of this kind stand in intimate connection with the theory of the formation of solutions and alloys and other so-called indefinite compounds.

[9] Moissan (1893) studied the compounds of Mo and W formed with carbon in the electric furnace (they are extremely hard) from a mixture of the anhydrides and carbon. Poleck and Grützner obtained definite compounds, FeW_2 and FeW_2C_3, for tungsten. Metallic W and Mo displace Ag from its solutions, but not Pb.

do not act on molybdenum, but when fused with it hydrogen is given off; which shows, as does its whole character, the acid properties of the metal. The properties of tungsten are almost identical; it is infusible, has an iron-grey colour, is exceedingly hard, so that it even scratches glass. Its specific gravity is 19·1 (according to Roscoe), or 18·7 (according to Moissan), so that, like uranium, platinum, &c., it is one of the heaviest metals.[9a] Just as sulphur and chromium have their corresponding persulphuric and perchromic acids, $H_2S_2O_8$ and $H_2Cr_2O_8$, having the properties of peroxides, and corresponding to peroxide of hydrogen, so also molybdenum and tungsten are known to give **permolybdic** and **pertungstic** acids, $H_2Mo_2O_8$ and $H_2W_2O_8$, which have the properties of true peroxides, i.e., they easily disengage iodine from KI and chlorine from HCl, easily part with their oxygen, and are formed by the action of peroxide of hydrogen, into which they are readily reconverted.[9b]

[9a] Tungsten and molybdenum form sulphides having an acid character, like carbon bisulphide or stannic sulphide. If sulphuretted hydrogen is passed through a solution of a molybdate it does not give a precipitate unless sulphuric acid is present, when a dark-brown precipitate of **molybdenum trisulphide**, MoS_3, is formed. When this sulphide is ignited without access of air it gives the bisulphide MoS_2; the latter is not able to combine with potassium sulphide like the trisulphide MoS_3, which forms a salt, K_2MoS_4, corresponding with K_2MoO_4. This is soluble in water, and separates out from its solution in red crystals, which have a metallic lustre and reflect a green light. It is easily obtained by heating the native bisulphide, MoS_2, with potash, sulphur, and a small amount of charcoal, which serves for deoxidising the oxygen compounds. Tungsten gives similar compounds, R_2WS_4, where $R = NH_4$, K, Na. They are decomposed by acids, with the separation of tungsten trisulphide, WS_3, and molybdenum trisulphide, MoS_3. Rideal (1892) obtained W_2N_3 by heating WO_3 in NH_3. This compound exhibited the general properties of metallic nitrides.

[9b] They may be regarded as compounds of H_2O_2 with $2MoO_3$ and $2WO_3$, &c. Their formation (Boerwald, 1884; Kemmerer, 1891) is at once seen in the coloration (not destroyed by boiling), which is obtained on mixing a solution of the salts with peroxide of hydrogen, and on treating, for instance, molybdic acid with a solution of peroxide of hydrogen (Péchard, 1892). The acid then forms an orange-coloured solution, which after evaporation *in vacuo* leaves $Mo_2H_2O_8,4H_2O$ as a crystalline powder, and loses $4H_2O$ at 100°, above which it decomposes with the evolution of oxygen. When peroxide of hydrogen acts upon a solution of potassium molybdate, well-formed yellow crystals belonging to the triclinic system separate out in the cold. When these crystals are heated *in vacuo* they first lose water and then decompose, leaving a residue composed of the salt originally taken. They are soluble in water but insoluble in alcohol. Their composition is represented by the formula $K_2Mo_2O_8,2H_2O$. A corresponding sodium pertungstate has been obtained by Péchard by boiling sodium tungstate with a solution of peroxide of hydrogen for several minutes. The solution rapidly turns yellow, and no longer gives a precipitate of tungstic acid when treated with nitric acid. When evaporated *in vacuo* the solution leaves a thick syrupy liquid from which stellate crystals separate out; these crystals are more soluble in water than the salt originally taken. Their composition answers to the formula $Na_2W_2O_8,2H_2O$. When treated with oxygen acids they give peroxide of hydrogen, and disengage chlorine and iodine from hydrochloric acid and potassium iodide.

Piccini (1891) showed that peroxide of hydrogen not only combines with the oxygen

Uranium, U=239, has the highest atomic weight of all the analogues of chromium, and indeed of all the elements yet known. Its highest salt-forming oxide, UO_3, shows very feeble acid properties. Although it gives sparingly soluble yellow compounds with alkalies, which fully correspond with the dichromates—for example, $Na_2U_2O_7 = Na_2O,2UO_3$ [10]—yet it more frequently and easily reacts with acids,

---

compounds of Mo and W, but also with their fluo-compounds, among which ammonium fluo-molybdate, $MoO_2F_2,2NH_4$, and others have long been known. The action of peroxide of hydrogen upon these compounds gives salts containing a larger amount of oxygen; for instance, a solution of $MoO_2F_2,2KF,H_2O$ with peroxide of hydrogen gives a yellow solution which after cooling deposits yellow crystalline flakes of $MoO_3F_2,2KF,H_2O$, resembling in their external appearance the salt originally taken.

If permolybdic acid be regarded as $2MoO_3 + H_2O_2$, i.e., as containing the elements of peroxide of hydrogen, then Piccini's compound will also be found to contain the original salts $+ H_2O_2$; for example, from $MoO_2F_2,2KF,H_2O$ there is obtained a compound $MoO_2F_2,2KF,H_2O_2$, i.e., instead of H_2O they contain H_2O_2. The capacity of the salts of molybdenum and tungsten to retain a further amount of oxygen or H_2O_2 probably bears some relation to their property of giving complex acids and of polymerising, which has been considered in note 8a.

[10] Uranium trioxide, or uranic oxide, shows its feeble basic and acid properties in many respects. (1) Solutions of uranic salts give yellow precipitates with alkalies, but these precipitates do not contain the hydrate, but compounds of it with bases; for example, $2UO_2(NO_3)_2 + 6KHO = 4KNO_3 + 3H_2O + K_2U_2O_7$. There are other **urano-alkali compounds** of the same constitution; for example, $(NH_4)_2U_2O_7$ (known commercially as uranic oxide), MgU_2O_7,BaU_2O_7. They are the analogues of the dichromates. Sodium uranate is the most generally used under the name of uranium yellow, $Na_2U_2O_7$. It is used for imparting the characteristic yellow-green tint to glass and porcelain. Neither heat nor water nor feeble acids are able to extract the alkali from sodium uranate, $Na_2U_2O_7$, and therefore it is a true insoluble salt, of a yellow colour, and clearly indicates the acid character (although feeble) of uranic oxide. (2) The carbonates of the alkaline earths (for instance, barium carbonate) precipitate uranic oxide from its salts, as they do all the salts of feeble bases, for example, R_2O_3. (3) The **alkaline carbonates**, when added to solutions of uranic salts, give a **precipitate, which is soluble in an excess of the reagent**, and particularly so if the acid carbonates are taken. This is due to the fact that (4) the uranyl salts **easily form double salts** with the salts of the alkali metals, including those of ammonium. Uranium, in the form of these double salts, often gives salts of well-defined crystalline form, although the simple salts are little prone to appear in crystals. Such, for example, are the salts obtained by dissolving potassium uranate, $K_2U_2O_7$, in acids, with the addition of potassium salts of the same acids. Thus, with hydrochloric acid and potassium chloride a well-formed crystalline salt, $K_2(UO_2)Cl_4,2H_2O$, belonging to the monoclinic system, is produced. This salt decomposes in dissolving in pure water. Among these double salts we may mention the double carbonate with the alkalies, $R_4(UO_2)(CO_3)_3$ (equal to $2R_2CO_3 + UO_2CO_3$); the acetates, $R(UO_2)(C_2H_3O_2)_3$, for instance, the sodium salt, $Na(UO_2)(C_2H_3O_2)_3$, and the potassium salt, $K(UO_2)(C_2H_3O_2)_3,H_2O$; the sulphates, $R_2(UO_2)(SO_4)_2,2H_2O$, &c. In the preceding formula $R = K$, Na, NH_4, or $R_2 = Mg$, Ba, &c. *This property of giving comparatively stable double salts indicates feebly developed basic properties*, because double salts are mainly formed by salts of distinctly basic metals (these form, as it were, the basic element of a double salt) and salts of feebly energetic bases (these form the acid element of a double salt). For this reason barium does not give double salts with alkalies as magnesium does, and this is why double salts are more easily formed by potassium than by lithium in the series of the alkali metals. (5) The most remarkable property, proving the feeble energy of uranic oxide as a base, is seen in the fact that

HX, forming fluorescent yellowish-green salts of the composition UO_2X_2, and in this respect uranic trioxide, UO_3, differs from chromic anhydride, CrO_3, although the latter is able to give the oxychloride, CrO_2Cl_2. In molybdenum and tungsten, however, we see a clear transition from chromium to uranium. Thus, for example, chromyl chloride, CrO_2Cl_2, is a brown liquid, which volatilises without change and is completely decomposed by water; molybdenum oxychloride, MoO_2Cl_2, is a crystalline substance of a yellow colour, volatile and soluble in water (Blomstrand), like many salts. Tungsten oxychloride, WO_2Cl_2, stands still nearer to uranyl chloride in its properties; it forms yellow scales on which water and alkalies act, as they do on many salts (zinc chloride, ferric chloride, aluminium chloride, stannic chloride, &c.), and corresponds perfectly with the difficultly volatile salt, UO_2Cl_2 (obtained by Peligot by the action of chlorine on ignited uranium dioxide, UO_2), which is also yellow and gives a yellow solution with water, like all the salts UO_2X_2. The property of uranic oxide, UO_3, of forming salts, UO_2X_2, is shown in the fact that the hydrated oxide of uranium, $UO_2(HO)_2$, which is obtained from the nitrate, carbonate, and other salts by the loss of the elements of the acid, is easily soluble in acids, as well as in the fact that the lower grades of oxidation of uranium are able, when treated with nitric acid, to form an easily crystallisable uranyl nitrate, $UO_2(NO_3)_2,6H_2O$; this is the most commonly occurring uranium salt.[11]

---

when their composition is compared with that of other salts those of uranic oxide **always appear as basic salts.** It is well known that a normal salt, R_2X_6, corresponds with the oxide R_2O_3, where $X=Cl$, NO_3, &c., or $X_2=SO_4$, CO_3, &c.; but there also exist basic salts of the same type, where $X=HO$ or $X_2=O$. We saw salts of all kinds among the salts of aluminium, chromium, and others. With uranic oxide no salts are known of the types UX_6 [UCl_6, $U(SO_4)_3$, alums, &c., are not known], nor even salts, $U(HO)_4X_2$ or UOX_4, but it always forms salts of the type $U(HO)_4X_2$ or UO_2X_2. Judging from the fact that nearly all the salts of uranic oxide retain water in crystallising from their solutions, and that this water is difficult to separate from them, it may be thought to be water of hydration. This is seen in part from the fact that the composition of many of the salts of uranic oxide may then be expressed without the presence of water of crystallisation; for instance, $U(HO)_4K_2Cl_4$ (and the salt of NH_4), $U(HO)_4K_2(SO_4)_2$; $U(HO)_4(C_2H_3O_2)_2$. Sodium uranyl acetate, however, does not contain water.

[11] **Uranyl nitrate,** or uranium nitrate, $UO_2(NO_3)_2,6H_2O$, crystallises from its solutions in transparent yellowish-green prisms (from an acid solution), or in tabular crystals (from a neutral solution), which effloresce in the air and are easily soluble in water, alcohol, and ether, have a sp. gr. of 2·8, and fuse when heated, losing nitric acid and water in the process. If the salt itself (Berzelius) or its alcoholic solution (Malaguti) is heated up to the temperature at which oxides of nitrogen are evolved, there then remains a mass which, after being evaporated with water, leaves uranyl hydroxide, $UO_2(HO)_2$ (sp. gr. 5·93), whilst if the salt is ignited there remains UO_3, as a brick-red powder, which on further heating loses oxygen and forms the dark-olive uranoso-uranic oxide, U_3O_8. The solution of the nitrate obtained from the ore is purified in the following manner: Sulphurous anhydride is first passed through it in order to reduce the arsenic acid present into arsenious acid; the solution is then heated to 60°, and sulphuretted

Uranium, which gives an oxide, UO_3, and the corresponding salt, UO_2X_2, and dioxide, UO_2, to which the salts UX_4 correspond, is rarely met with in nature. Uranite or the double orthophosphate of uranic oxide, $R(UO_2)H_2P_2O_8,7H_2O$, where $R=Cu$ or Ca, uranium-vitriol, $U(SO_4)_2,H_2O$, samarskite, and æschynite, are very rarely found, and then only in small quantities. Of more frequent and abundant occurrence is the non-crystalline earthy brown uranium ore known as **pitchblende** (sp. gr. 7·2), which is mainly composed of the intermediate oxide, $U_3O_8=UO_2,2UO_3$. This ore is found at Joachimsthal (in Bohemia) and in Cornwall. It usually contains a number of different impurities, chiefly sulphides and arsenides of lead and iron, as well as lime and silica compounds. In order to expel the arsenic and sulphur, it is roasted, ground, washed with dilute hydrochloric acid, which does not dissolve the uranoso-uranic oxide, U_3O_8, and the residue is dissolved in nitric acid, which transforms the uranium oxide into the nitrate, $UO_2(NO_3)_2$.

It must be observed that the oxide of uranium, first distinguished by Klaproth (1789), was for a long time regarded as able to give metallic uranium under the action of charcoal and other reducing agents (with the aid of heat). But the substance thus obtained was only the **uranium dioxide**, UO_2. The compound nature of this dioxide,[12] or the

hydrogen passed through it; this precipitates the lead, arsenic, and tin, and certain other metals. This liquid is then filtered and evaporated with nitric acid to crystallisation, and the crystals are dissolved in ether. Or else the solution is first treated with chlorine in order to convert the ferrous chloride (produced by the action of the hydrogen sulphide) into ferric chloride, the oxides are then precipitated by ammonia, and the resultant precipitate, containing the oxides Fe_2O_3,UO_3, and compounds of the latter with potash, lime, ammonia, and other bases present in the solution (the latter being due to the property of uranic oxide of combining with bases), is washed and dissolved in a strong, slightly heated solution of ammonium carbonate, which dissolves the uranic oxide, but not the ferric oxide. The solution is filtered, and on cooling deposits a well-crystallising **uranyl ammonium carbonate**, $UO_2(NH_4)_4(CO_3)_3$, in brilliant monoclinic crystals which on exposure to air slowly give off water, carbonic anhydride, and ammonia; the same decomposition is readily effected at 300°, the residue then consisting of uranic oxide. This salt is not very soluble in water, but is readily so in ammonium carbonate; it is obvious that it may readily be converted into all the other salts of oxides of uranium. Uranium salts are also purified in the form of *acetate*, which is very sparingly soluble, or as *oxalate*, which is very difficulty soluble, and is therefore directly precipitated from a strong solution of the nitrate by mixing it with oxalic acid.

We may also mention the **uranyl phosphate**, $HUPO_6$, which must be regarded as an orthophosphate in which two hydrogens are replaced by the radicle uranyl, UO_2, i.e., as $H(UO_2)PO_4$. This salt is formed as a hydrated gelatinous yellow precipitate, on mixing a solution of uranyl nitrate with disodium phosphate.

[12] Uranium dioxide, or **uranyl**, UO_2, which is contained in the salts UO_2X_2, has the appearance and many of the properties of a metal. Uranic oxide may be regarded as uranyl oxide, $(UO_2)O$, and its salts as salts of this uranyl; its hydroxide, $(UO_2)H_2O_2$, is constituted like CaH_2O_2. The green oxide of uranium, uranoso-uranic oxide (easily formed from uranic salts by the loss of oxygen), $U_3O_8=UO_2,2UO_3$, when heated with

presence of oxygen in it, was demonstrated by Peligot (1841) by igniting it with charcoal in a stream of chlorine. He thus obtained the corresponding volatile **uranium tetrachloride,** UCl_4,[13] which, when heated with sodium, gave **metallic uranium** as a grey metal, having a specific gravity of 18·7,[14] and liberating hydrogen from acids, with the

---

charcoal or hydrogen (dry) gives a brilliant crystalline UO_2 of sp. gr. about 11·0 (Urlaub), which has an appearance resembling that of metals, and decomposes steam at a red heat with the evolution of hydrogen; it does not, however, decompose hydrochloric or sulphuric acid, but is oxidised by nitric acid. The same substance (i.e., uranium dioxide, UO_2) is also obtained by igniting the compound $(UO_2)K_2Cl_4$ in a stream of hydrogen, according to the equation, $UO_2K_2Cl_4 + H_2 = UO_2 + 2HCl + 2KCl$. It was at first regarded as the metal. In 1841 Peligot found that it contained oxygen, because carbonic oxide and anhydride were evolved when it was ignited with charcoal in a stream of chlorine, and from 272 parts of the substance which was considered to be metal he obtained 382 parts of a volatile product containing 142 parts of chlorine. From this it was concluded that the substance taken contained an equivalent amount of oxygen. As 142 parts of chlorine correspond with 32 parts of oxygen, it followed that $272 - 32 = 240$ parts of metal were combined in the substance with 32 parts of oxygen, and also in the chlorine compound obtained with 142 parts of chlorine. These calculations have been made for the now accepted atomic weight of uranium.

[13] **Uranium tetrachloride**, uranous chloride, UCl_4, corresponds with uranous oxide, UO_2, as a base. It was obtained by Peligot by igniting uranic oxide mixed with charcoal in a stream of *dry* chlorine: $UO_3 + 3C + 2Cl_2 = UCl_4 + 3CO$. This green volatile compound (note 12) crystallises in regular octahedra, is very hygroscopic, easily soluble in water with the development of a considerable amount of heat, and no longer separates out from its solution in an anhydrous state, but disengages hydrochloric acid when evaporated. The solution of uranous chloride in water is green. It is also formed by the action of zinc and copper (forming cuprous chloride) on a solution of uranyl chloride, UO_2Cl_2, especially in the presence of hydrochloric acid and sal-ammoniac. Solutions of uranyl salts are converted into uranous salts by the action of various reducing agents, and among others by organic substances or by the action of light, whilst the salts UX_4 are converted into uranyl salts, UO_2X_2, by exposure to air or by oxidising agents. Solutions of the green uranyl salts act as powerful reducing agents, and give a brown precipitate of the uranous hydroxide, UH_4O_4, with potash and other alkalies. This hydroxide is easily soluble in acids but not in alkalies. On ignition it does not form the oxide UO_2, because it decomposes water, but when the higher oxides of uranium are ignited in a stream of hydrogen or with charcoal they yield uranous oxide. Both it and the chloride UCl_4 dissolve in strong sulphuric acid, forming a green salt, $U(SO_4)_2,2H_2O$. The same salt, together with uranyl sulphate, $UO_2(SO_4)$, is formed when the green oxide, U_3O_8, is dissolved in hot sulphuric acid. The salts obtained in the latter instance may be separated by adding alcohol to the solution, which is left exposed to the light; the alcohol reduces the uranyl salt to uranous salt, an excess of acid being required. An excess of water decomposes this salt, forming a basic salt, which is also easily produced under other circumstances, and consists of $UO(SO_4),2H_2O$ (which corresponds to the uranic salt). According to Orloff (1902), green crystals of $U(SO_4)_2,8H_2O$, previously obtained by Rammelsberg, are formed if an alcoholic or acidulated (with H_2SO_4) solution of UO_2SO_4 is exposed to the sun's rays (reduction takes place). Concerning the peroxide of uranium or peruranic anhydride, UO_4, see Chap. XX., note 66.

[14] The atomic weight of uranium was formerly taken as half the present one, $U = 120$, and the oxides U_2O_3, suboxide UO, and green oxide U_3O_4, were of the same types as the oxides of iron. With a remote resemblance to the elements of the iron group, uranium presents many points of distinction which do not permit its being grouped with them.

The alteration or doubling of the atomic weight of uranium—i.e., the recognition of $U = 240$—was made for the first time in the first (Russian) edition of this work (1871), on formation of green uranous salts, UX_4, which act as powerful reducing agents.[14a]

As the salts of uranic oxide are reduced in the absence of organic matter by the action of light, and as they impart a characteristic coloration to glass,[15] they find a certain application to photography and glass work.[15a]

the ground that with an atomic weight 120, uranium could not be placed in the periodic system. I think it will not be superfluous to add that—(1) in the other groups (K—Rb—Cs, Ca—Sr—Ba, Cl—Br—I) the acid character of the oxides decreases and their basic character increases with the rise of atomic weight, and therefore we should expect to find the same in the group Cr—Mo—W—U, and if CrO_3, MoO_3, WO_3 be the anhydrides of acids then we indeed find a decrease in their acid character, and therefore uranium trioxide, UO_3, should be a very feeble anhydride, but its basic properties should also be very feeble. Uranic oxide does indeed show these properties, as was pointed out above (note 10). (2) Chromium and its analogues, beside the oxides RO_3, also form lower grades of oxidation RO_2,R_2O_3, and the same is seen in uranium; it forms UO_3, UO_2, U_2O_3 and their compounds. (3) Molybdenum and tungsten, in being reduced from RO_3, easily and frequently give an intermediate oxide of a blue colour, and uranium shows the same property, giving the so-called green oxide which, according to present views, must be regarded as $U_3O_8 = UO_2,2UO_3$, analogous to Mo_3O_8. (4) The higher chlorides, RCl_6, possible for the elements of group VI. are either unstable (WCl_6) or do not exist at all (Cr); but there is one single lower volatile compound, which is decomposed by water, and is liable to further reduction into a non-volatile chlorine product and the metal. The same is observed in uranium, which forms an easily volatile chloride, UCl_4, decomposed by water. (5) The high sp. gr. of uranium (18·6) is explained by its analogy to tungsten (sp. gr. 19·1). (6) For uranium, as for chromium and tungsten, yellow tints predominate in the form RO_3, whilst the lower forms are green and blue. (7) Zimmermann (1881) determined the vapour densities of uranous bromide, UBr_4, and chloride, UCl_4, and they were found to correspond to the formulæ given above—that is, they confirmed the higher atomic weight, U = 240. Roscoe, a great authority on the metals of this group, was the first to accept the proposed atomic weight of uranium, U = 240, which since Zimmermann's work has been generally recognised.

[14a] Uranium forms C_3U_2 in the electric furnace (1,000 ampères, 50 volts) with an excess of carbon. This carbide acts upon water with the formation of gaseous (CH_4,C_2H_2, &c.) and liquid hydrocarbons (Moissan, 1896).

[15] Uranium glass, obtained by the addition of the yellow salt, $K_2U_2O_7$, to glass, has a greenish-yellow fluorescence, and is sometimes employed for ornaments; it absorbs the violet rays, like the other salts of uranic oxide—that is, it possesses an absorption spectrum in which the violet rays are absent. The index of refraction of the absorbed rays is altered, and they are given out again as greenish-yellow rays; hence compounds of uranic acid, when placed in the violet portion of the spectrum, emit a greenish-yellow light, and this forms one of the best examples (another is found in a solution of quinine sulphate) of the phenomenon of fluorescence. The rays of light which pass through uranic compounds do not contain the rays which excite the phenomena of fluorescence and of chemical transformation, as is proved by the researches of Stokes.

[15a] Uranium stands out from all other known chemical elements in having the greatest atomic weight, and although belonging to the 12th series of group VI. (see Preface), in not having any known elements surrounding it in the periodic system. Thus neither VI. 11, VI. 13, V. 12, nor VII. 12 is known. Now, when the periodic law has been confirmed from the most varied aspects, it appears to me that there is much significance in these facts concerning uranium, more particularly since its connection with two of the most important—in many respects—discoveries in physics and chemistry made in our days, i.e., the discovery of the argon elements (especially of helium) and of the radio-active substances. Both present much that is unexpected and extreme in some yet

If we compare among the acid elements of group VI., sulphur, selenium, and tellurium, of the uneven series, with chromium,

deeply hidden way, connected with the extreme nature of the evolution of the elements of uranium itself. The greatest known concentration of mass of ponderable matter in the indivisible mass of the atom of uranium should already, *a priori*, produce peculiar qualities, although I am not in any way inclined (owing to the stern but fruitful discipline of inductive knowledge) to admit even the hypothetical transmutation of the elements into each other, and see no possibility of the argon or radio-active substances having originated from uranium or conversely. Being convinced that the investigation of uranium, starting from its native sources, will lead to many new discoveries, I am bold enough to recommend those who seek new subjects of research to occupy themselves with the uranium compounds, and may add that, for me personally, uranium has special interest owing to the prominent part it played in confirming the periodic law, inasmuch as its atomic weight, U = 240, was changed from U = 120 on the basis of this law, and was subsequently confirmed by experiment (Roscoe, Rammelsberg, Zimmermann, and others), which (together with the atomic weights of Ce and Be) convinced me of the universality of the law. Unfortunately the native minerals of uranium are not within the reach of many, owing to their extreme rarity.

Radio-active substances. In 1896 H. Becquerel discovered that uranium compounds have the faculty of emitting peculiar invisible rays (like the Röntgen and cathodic rays) which are given off constantly and independently without any visible expenditure of external energy (a marked difference from the Röntgen and cathodic rays). These rays are capable, (*a*) of producing, although somewhat slowly, chemical changes of various kinds, such as acting on a photographic plate and forming an image (which can be developed like an ordinary photograph), of tinting glass violet or brown (the coloration proceeds slowly but is permanent), of even ozonising air, &c.; (*b*) of penetrating through opaque bodies, for instance, through black paper, thin metallic discs, wood, &c. (this faculty for penetration is not quite alike for all radio-active rays, so that the latter cannot be considered as always uniform); (*c*) of causing such phosphorescent substances as zinc sulphide, barium platino-cyanide, &c., to become luminous in the dark (a considerable amount of radio-active matter is required to render this quite evident); (*d*) of rendering bodies subjected to these rays themselves temporarily (and sometimes for a considerable period) radio-active (this is a sort of induction, a temporary radio-activity. For instance, many of the objects in the laboratories, where much work has been done with these substances, acquire the same faculty, and the air no longer serves as an insulator); and (*e*) of communicating to the air, through which these rays pass, the faculty of rapidly causing electric discharges (in electroscopes*). The last property was chiefly investigated by Rutherford and Madame Curie, and gives the possibility of measuring the degree of radio-activity of substances, for, other conditions being similar (for instance, the pressure of the air), the faculty of discharging generally depends, not on the thickness of the layer of the radio-active substance, but only on its superficial area, the thickness of the layer of air, and the radio-activity of the substance under investigation, even in solution. In this respect it should be mentioned that the substances isolated by artificial means (as subsequently described) are hundreds of times more active than the native uranium minerals.

The unlooked-for peculiarity of the newly discovered properties incited many (and especially Professor and Madame Curie, Rutherford, Afanasieff, Giselle, and others) to follow Becquerel's example, and seek for radio-activity in different minerals and chemical reagents. It was at once found that this faculty belongs almost exclusively to the compounds of the two elements uranium and thorium, which are distinguished according to the periodic law by the fact that they possess the highest atomic weights of all the elements. It is particularly characteristic that the radio-activity is almost quite

---

* Phosphorus, in oxidising in damp air, also endows it with this property, or, as it is commonly said, ozonises the air. Le Bon (1900) observed that anhydrous sulphate of quinine, in absorbing moisture from the air, also ozonises it.

molybdenum, tungsten, and uranium, of the even series, we find that

independent of preliminary illumination, and in this respect is distinctly different from phosphorescence. Substances taken direct out of a mine or kept for a long time in darkness are just as radio-active as those which have been lying in the sunlight. A change of temperature also has little effect on the radio-activity. Metallic uranium fused in the electric furnace is as radio-active as that freshly prepared, but the activity apparently increases at the temperature of liquid air.

In general the radio-activity proved to be almost proportional to the amount of uranium or thorium present, so that the metal is more active than any of the compounds of uranium. But as some of the native uranium minerals, such as uranium copper ore, known as chalcolite, and some sorts of pitchblende, were found to be more radio-active than would follow from the proportion of uranium they contained, and even more active than the metal itself, and it was always possible to separate a more radio-active substance by fractionation, Professor and Madame Curie come to the conclusion that there must be a series of peculiar radio-active elements. So far three such elements are recognised: **radium**, which resembles barium; **polonium**, resembling bismuth; and **actinium**, resembling thorium (it separates out with iron); but of these, only radium has been obtained with any degree of purity. The compounds of radium, polonium, and actinium were extracted from the residues obtained in treating the uranium and thorium ores, but they are present in such small amounts that hardly more than a few decigrams of chloride of radium have yet been procured in a pure state from several tons of pitchblende. Uranium pitchblende has a very complex composition and contains a number of elements, in the separation of which, substances reacting like barium, bismuth, and thorium are also obtained, and it is these that contain the above radio-active elements. Thus, for example, polonium is separated together with bismuth, and if it is converted into sulphide of bismuth the first portions of the sublimate are found to be more radio-active and are regarded as a compound of polonium. Polonium is precipitated by H_2S from a very acid solution before bismuth, and is also precipitated from a nitric acid solution by water before the bismuth; antimony also deposits it from its solutions (Marckwald, 1902). Actinium was recognised by Debierne and separates out together with thorium, but it is precipitated before the latter by sodium hyposulphite and also by peroxide of hydrogen. **Radium** was obtained in the state of greatest purity by Professor and Madame Curie (in 1899–1902) by a process depending on the fact that chloride of radium is more soluble in water, alcohol, and hydrochloric acid than barium chloride. Carbonate of ammonium precipitates the radium carbonate only after the barium has been precipitated. Demarçay investigated the spectrum of radium and found it to resemble those of the metals of the alkaline earths; the most prominent lines (not proper to barium) given by the spark spectrum had wave-lengths of 482·6, 468·3, 453·3, 434·1, 381·5, and 365·0 millionths of a millimetre. Radium colours the flame carmine-red (Giselle). In 1902, Madame Curie found that the atomic weight of radium in its purest state was 223–225, or on the average about 224, if its chloride be given the composition $RdCl_2$. This places it in group II., in the 12th series of the periodic system. The pure salt in a crystalline form is colourless and emits light in the dark; the crystals turn yellow or rose-colour after a time, but if redissolved again form colourless crystals. $RdBr_2$, in ozonising the air, becomes alkaline, and Giselle (1902) then observed the formation of a highly radio-active gas which was not investigated. Further information respecting the chemical properties of the radio-active elements has not yet been obtained, and it should be mentioned that the existing data give some reason, if not for doubting the existence of the separate elements named above, at all events for not attributing radio-activity exclusively to them; that is, to regard it as a special state of matter rather than a property belonging exclusively to the atoms of certain elements, especially as this property at first appeared to belong to uranium * and thorium. More-

---

* Crookes considers that he obtained uranium quite free from radio-activity by subjecting the oxalate to fractional crystallisation.

the resemblance of the properties of the higher form, RO_3, does not extend to the lower forms, and even entirely disappears in the elements, for there is not the smallest resemblance between sulphur and chromium and their analogues, in a free state. In other words, this means that the small periods, like Na, Mg, Al, Si, P, S, Cl, containing seven elements, do not contain any near analogues of chromium, molybdenum, &c., and therefore their true position among the other elements must be looked for only in those large periods which contain two small periods, and whose type is seen in the period containing: K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br. These large periods contain Ca and Zn, giving RO; Sc and Ga of the third group, Ti and Ge giving RO_2; V and As forming R_2O_5; Cr and Se of the sixth group, Mn and Br of the seventh group, the remaining elements, Fe, Co, Ni, forming connective members of the intermediate eighth group, to the description of the representatives of which we shall turn in the following chapters. We shall now proceed to describe **manganese**, Mn=55, as an element of the seventh group of the even series, directly following after Cr=52, which corresponds with Br=80 to the same degree that Cr does with Se=79. For chromium, selenium, and bromine very close analogues are known, but for manganese as yet none have

over, Giselle showed that the radio-activity of preparations of radium increases with time, while in the case of polonium it decreases (like that of an induced body). Rutherford, by precipitating a solution of thorium with ammonia, almost to the end, obtained a residue which had a more intense activity, which it lost, however, in the course of time, although the precipitate of the chief mass of the hydrate of thorium was only slightly active at the beginning and gradually rose. Hofmann (1902) obtained preparations of uranium, &c., which had no radio-activity at all, but acquired it after being kept some time in a closed vessel. It is most remarkable that a copper or aluminum wire, electrified at the negative poles of a powerful Ruhmkorff's coil (having a potential of several thousand volts) becomes radio-active on its surface (Elster and Geitel, 1902), and that, if this superficial portion be removed, it gives a radio-active substance. In my opinion radio-activity must so far be regarded as a *property or state* into which many (but hardly all) substances may be brought, just as certain substances can be magnetised, and that radio-active substances may be looked upon as those which are able to pass into that state just as iron, steel, and cobalt can be magnetised. Moreover, it appears to me that radio-activity is probably connected with the power of a substance to absorb from, and emit into, the surrounding spaces some peculiar unknown substance, allied perhaps to that which forms ether of space and permeates all bodies. Two circumstances seem more especially to indicate that this is so: in the first place helium, argon, and the accompanying gases are found in a peculiar state (see Chap. V., p. 252) in the uranium and thorium minerals, and these gases apparently form a sort of transition to the substance which occupies space, as is seen from observations made on the solar corona, the aurora borealis, and similar phenomena; and in the second place Professor and Madame Curie and others, by heating native uranium compounds, obtained a gas which possessed radio-active properties, but not permanently. But in general this subject forms one of the most brilliant, and at the same time mysterious, discoveries of the close of the nineteenth century, and it is to be hoped that its elaboration (it is being studied by many men of science) will greatly help towards a true explanation of the existing data on light and electricity, and also ether.

been obtained—that is, it is the only representative of the even series in the seventh group. In placing manganese with the halogens in one group, the periodic system of the elements only requires that it should bear an analogy to the halogens in the higher type of oxidation—i.e., in the salts and acids—whilst it requires that as great a difference should be expected in the lower types and elements as there exists between chromium and sulphur or molybdenum and selenium. And this is actually the case. The elements of the seventh group form a higher salt-forming oxide, R_2O_7, and its corresponding hydrate, HRO_4, and salts—for example, $KClO_4$. Manganese in the form of potassium permanganate, $KMnO_4$, actually presents a great analogy in many respects to potassium perchlorate, $KClO_4$. The analogy of the crystalline form of both salts was shown by Mitscherlich. The salts of permanganic acid are also nearly all soluble in water, like those of perchloric acid, and if the silver salt of the latter, $AgClO_4$, is sparingly soluble in water, so also is silver permanganate, $AgMnO_4$. The specific volume of potassium perchlorate is equal to 55, because its specific gravity is 2·54; the specific volume of potassium permanganate is equal to 58, its specific gravity being 2·71. So that the volumes of equivalent quantities are in this instance approximately the same, whilst the atomic volumes of chlorine ($35{\cdot}5/1{\cdot}3=27$) and manganese ($55/7{\cdot}5$) are in the ratio 4 : 1. In a free state the higher acids, $HClO_4$ and $HMnO_4$, are both soluble in water and volatile, both are powerful oxidisers—in a word, their analogy is still closer than that of chromic and sulphuric acids, and those points of distinction which they present also appear among the nearest analogues—for example, in sulphuric and telluric acids, in hydrochloric and hydriodic acids, &c. Besides Mn_2O_7, manganese gives a lower degree of oxidation, MnO_3, analogous to sulphuric and chromic trioxides, and with it corresponds potassium manganate, K_2MnO_4, isomorphous with potassium sulphate.[16] In the still lower grades of oxidation, Mn_2O_3 and MnO, there is hardly any similarity to chlorine, whilst every point of resemblance disappears when we come to the elements themselves—i.e., to manganese and chlorine—for manganese is a metal, like iron, which combines directly with chlorine to form a saline compound, $MnCl_2$, analogous to magnesium chloride.[17]

---

[16] The comparison of potassium permanganate with potassium perchlorate, or of potassium manganate with potassium sulphate, shows directly that many of the physical and chemical properties of substances do not depend on the nature of the elements, but on the atomic types in which they appear, on the kind of movements, or on the positions in which the atoms forming the molecule occur.

[17] If, however, we compare the spectra (Vol. I., p. 582) of chlorine, bromine, and iodine with that of manganese, a certain resemblance or analogy is to be found connecting manganese both with iron and with chlorine, bromine, and iodine.

Manganese belongs to the metals which are widely distributed in nature, especially in those localities where iron occurs, the ores of the latter frequently containing compounds of manganous oxide, MnO, which presents a resemblance to ferrous oxide, FeO, and to magnesia. In many minerals magnesia and the oxides allied to it are replaced by manganous oxide; calc spars and magnesites—i.e., $R''CO_3$ in general—are frequently met with containing manganous carbonate, which also occurs in a separate state, although but rarely. The soil also and the ash of plants generally contain a small quantity of manganese. In the analysis of minerals it is generally found that manganese occurs together with magnesia, because, like it, manganous oxide remains in solution in the presence of ammoniacal salts, not being precipitated by reagents. The property of this manganous oxide, MnO, of passing into the higher grades of oxidation under the influence of heat, alkalies, and air gives an easy means not only of discovering the presence of manganese in admixture with magnesia, but also of separating these two analogous bases. Magnesia is not able to give higher grades of oxidation, whilst manganese gives them with great facility. Thus, for instance, an *alkaline* solution of sodium hypochlorite produces a precipitate of manganese dioxide in a solution of a manganous salt: $MnCl_2 + NaClO + 2NaHO = MnO_2 + H_2O + 3NaCl$; whilst magnesia is not changed under these circumstances, and remains in the form of $MgCl_2$. If the magnesia be precipitated owing to the presence of alkali, it may be dissolved in acetic acid, in which manganese dioxide is insoluble. The presence of small quantities of manganese may also be recognised by the green coloration which alkalies acquire when heated with manganese compounds in the air. This green coloration depends on the property of manganese of forming a still higher oxide and giving a green alkaline manganate corresponding to MnO_3: $MnCl_2 + 4KHO + O_2 = K_2MnO_4 + 2KCl + 2H_2O$. Thus **the faculty of oxidising in the presence of alkalies** forms an essential character of manganese. The higher grades of oxidation containing Mn_2O_7 and MnO_3 are quite unknown in nature, and even MnO_2 is not so widely spread in nature as the ores composed of manganous compounds, which are met with nearly everywhere. The most important ore of manganese is its **dioxide**, or so-called **peroxide**, MnO_2, which is known in mineralogy as **pyrolusite** (a black powder of sp. gr. 4·2). Manganese also occurs as an oxide corresponding with magnetic iron ore, $MnO,Mn_2O_3 = Mn_3O_4$, forming the mineral known as **hausmannite** (sp. gr. 4·3; brown powder). The oxide Mn_2O_3 also occurs in nature as the anhydrous mineral **braunite**, and in a hydrated form, Mn_2O_3,H_2O, called **manganite.** Both of these often occur as an admixture in pyrolusite. Besides which, manganese is met with in nature as a rose-coloured mineral, **rhodonite**, or silicate, $MnSiO_3$. Very fine and rich deposits of manganese ores have been found in the Caucasus, the Urals, and along the Dnieper. Those in the Sharapansky district of the government of Kutais and at Nicopol on the Dnieper are particularly rich. A large quantity of the ore (as much as 180,000 tons yearly) is exported from these localities.

Thus, manganese gives oxides of the following forms: MnO, manganous oxide, and manganous salts, MnX_2, corresponding with the base, which resembles magnesia and ferrous oxide in many respects; Mn_2O_3, a very feeble base, giving salts, MnX_3, analogous to the aluminium and ferric salts, easily reduced to MnX_2; MnO_2, dioxide, an almost indifferent or feebly acid oxide;[18] MnO_3, manganic anhydride, which forms salts resembling potassium sulphate;[18a] Mn_2O_7, permanganic anhydride, giving salts analogous to the perchlorates.

All the oxides of manganese when heated with acids give salts, MnX_2, corresponding with the lower grade of oxidation, **manganous oxide,** MnO. Manganic oxide, Mn_2O_3, is a feebly energetic base; it is true that it dissolves in hydrochloric acid and gives a dark solution containing the salt $MnCl_3$, but the latter when heated evolves chlorine and gives a salt corresponding with manganous oxide, $MnCl_2$—i.e., at first: $Mn_2O_3+6HCl=3H_2O+Mn_2Cl_6$, and then the Mn_2Cl_6 decomposes into $2MnCl_2+Cl_2$. None of the remaining higher grades of oxidation have a basic character, but **act as oxidising agents in the presence of acids,** disengaging oxygen and passing into salts, MnX_2. Owing to this circumstance, **the manganous salts,** MnX_2, are often obtained; they are, for instance, left in the residue when the dioxide is used for the preparation of oxygen and chlorine.[19]

---

[18] Bisulphide of manganese, MnS_2, corresponding to iron pyrites, FeS_2, sometimes occurs in nature in fine octahedra (and cube combinations), for instance, in Sicily; it is called hauerite.

[18a] On comparing the empirical composition of the manganates and the permanganates —for example, K_2MnO_4 with $KMnO_4$—we find that they differ by one equivalent of the metal. Such a relation in composition produced by oxidation is of frequent occurrence —for instance, $K_4Fe(CN)_6$ in oxidising gives $K_3Fe(CN)_6$; H_2O forms HO or H_2O_2, &c.

[19] In the preparation of oxygen from the dioxide by means of H_2SO_4, $MnSO_4$ is formed; in the preparation of chlorine from HCl and MnO_2, $MnCl_2$ is obtained. It generally contains various impurities, and also a large amount of iron salts (from the native MnO_2), from which it cannot be freed by crystallisation. $MnSO_4$ is purified by mixing a portion of the liquid with a solution of sodium carbonate; a precipitate of manganous carbonate is then formed. This precipitate is collected and washed, and then added to the remaining mass of the impure solution of manganous sulphate; on heating the solution with this precipitate, the whole of the iron is precipitated as oxide. This is due to the fact that in the solution of the manganese dioxide in sulphuric acid the whole of the iron is converted into the ferric state (because the dioxide acts as an oxidising agent), which, as an exceedingly feeble base, precipitated by calcium carbonate and other kindred salts, separates out together with manganous carbonate. After being treated in this manner, the solution of manganous sulphate is easily purified by crystalli-

As the salts of manganous oxide closely resemble (and are isomorphous with) the salts of magnesia, MgX_2, in many respects (with

sation. If it has a bright-red colour, this is due to the presence of higher grades of oxidation of manganese; they may be destroyed by boiling the solution, when the oxygen from the oxides of manganese is evolved and a very faintly coloured solution of manganous sulphate is obtained. This salt is remarkable for the facility with which it gives various combinations with water. By evaporating the almost colourless solution of **manganous sulphate** at very low temperatures, and by cooling the saturated solution at about 0°, crystals are obtained containing 7 atoms of water of crystallisation, $MnSO_4,7H_2O$, which are isomorphous with cobaltous and ferrous sulphates. These crystals, even at 10°, lose 5 per cent. of water, and completely effloresce at 15°, losing about 20 per cent. of water. By evaporating a solution of the salt at the ordinary temperature, but not above 20°, crystals are obtained which contain 5 mols. of H_2O and are isomorphous with copper sulphate, whilst if the crystallisation is carried on between 20° and 30°, large transparent prismatic crystals are formed containing 4 mols. of H_2O (see Nickel). A boiling solution also deposits these crystals together with others containing $3H_2O$, whilst the first salt, when fused and boiled with alcohol, gives crystals containing 2 mols. of H_2O. Graham obtained a monohydrated salt by drying the salt at about 200°. The last atom of water is eliminated with difficulty, as is the case with all salts like $MgSO_4,nH_2O$. The crystals containing a considerable amount of water are rose-coloured, and the anhydrous crystals colourless. The solubility of $MnSO_4,4H_2O$ (Chap. I., note 24) per 100 parts of water is: at 10°, 127 parts; at 37·5°, 149 parts; at 75°, 145 parts; and at 101°, 92 parts. Whence it is seen that at the boiling-point this salt is less soluble than at lower temperatures, and therefore a solution saturated at the ordinary temperature becomes turbid when boiled. Manganous sulphate, being analogous to magnesium sulphate, is decomposed, like the latter, when ignited; but it does not then leave manganous oxide, but the intermediate oxide, Mn_3O_4. It gives double salts with the alkali sulphates. With aluminium sulphate it forms fine radiated crystals, whose composition resembles that of the alums—namely, $MnAl_2(SO_4)_4,24H_2O$. This salt is readily soluble in water, and occurs in nature.

Manganous chloride, $MnCl_2$, crystallises with 4 mols. H_2O, like the ferrous salt, and not with 6 mols. like many kindred salts—for example, those of cobalt, calcium, and magnesium; 100 parts of water dissolve 38 parts of the anhydrous salt at 10° and 55 parts at 62°. Alcohol also dissolves manganous chloride, and the alcoholic solution burns with a red flame. This salt, like magnesium chloride, readily forms double salts. A solution of borax gives a dirty rose-coloured precipitate having the composition $MnH_4(BO_3)_2,H_2O$, which is used as a drier in paint-making. Potassium cyanide produces a yellowish-grey precipitate, MnC_2N_2, with manganous salts, soluble in an excess of the reagent, a double salt, $K_4MnC_6N_6$, corresponding with potassium ferrocyanide being formed (Chap. XXII.). On evaporation of this solution, a portion of the manganese is oxidised and precipitated, whilst a salt corresponding to Gmelin's red salt, $K_3MnC_6N_6$ (see Chap. XXII.), remains in solution. Sulphuretted hydrogen does not precipitate salts of manganese, not even the acetate, but ammonium sulphide gives a flesh-coloured precipitate, MnS; at 320° this sulphide of manganese passes into a green variety (Antony). Oxalic acid in strong solutions of manganous salts gives a white precipitate of the oxalate, MnC_2O_4. This precipitate is insoluble in water, and is used for the preparation of manganous oxide itself, because it decomposes like oxalic acid when ignited (in a tube without excess of air), with the formation of carbonic anhydride, carbonic oxide, and manganous oxide. **Manganous oxide** thus obtained is a green powder, which, however, oxidises with such facility that it burns in air when brought into contact with an incandescent substance, and passes into the red intermediate oxide, Mn_3O_4. In solutions of manganous salts, alkalies produce a precipitate of the hydroxide, MnH_2O_2, which rapidly absorbs oxygen in the presence of air and gives the brown intermediate oxide (hydrate). Manganous oxide, besides being obtained by the above-described method from manganous oxalate, may likewise be obtained by igniting the higher oxides in a stream of the exception of the fact that MnX_2 are rose-coloured and are easily oxidised in the presence of alkalies), we shall not dwell upon them, but limit ourselves to illustrating the chemical character of manganese by describing the metal and its corresponding acids. The single fact that the oxides of manganese are not reduced to the metal when ignited in

---

hydrogen, and also from manganese carbonate. The manganous oxide ignited in the presence of hydrogen acquires a great density, and is no longer so easily oxidised. It may also be obtained in a crystalline form, if during the ignition of the carbonate or higher oxide a trace of dry hydrochloric acid gas be passed into the current of hydrogen. It is thus obtained in the form of transparent emerald-green crystals of the regular system, and in this state is easily soluble in acids.

Manganous oxide, in oxidising, gives the **red oxide of manganese**, Mn_3O_4. This is the most stable of all the oxides of manganese; it is not only stable at the ordinary, but also at a high, temperature—that is, it does not absorb or disengage oxygen spontaneously. This oxide does not give any distinct salts, but it dissolves in sulphuric acid, forming a dark-red solution, which contains both manganous and manganic (of the **oxide**, Mn_2O_3) sulphates. The latter with potassium sulphate gives a manganese alum, in which the alumina is replaced by the isomorphous oxide of manganese. But this alum, like the solution of the intermediate oxide in sulphuric acid, evolves oxygen and leaves a manganous salt when slightly heated. Treated with nitric acid, Mn_2O_3 leaves MnO_2 (like red lead), and therefore Mn_2O_3 may be regarded as MnO,MnO_2.

Manganese dioxide, MnO_2, is still less basic than the oxide, and disengages oxygen or a halogen in the presence of acids, forming manganous salts, like the oxide. However, if it is suspended in ether, and hydrochloric acid gas passed into the mixture, which is kept cool, the ether acquires a green colour, owing to the formation of *tetrachloride of manganese*, $MnCl_4$ (corresponding with the dioxide), which passes into solution. It is, however, very unstable, being exceedingly easily decomposed, with the evolution of chlorine (Verron). The corresponding fluoride, MnF_4, obtained by Nicklés is much more stable (because fluorine bears a greater resemblance to oxygen than chlorine). Nicklés obtained the fluoride by the action of RF on MnO_2; it forms double salts, like K_2MnF_6. Manganese dioxide has rather an acid character, which is shown particularly in the compounds MnF_4 and $MnCl_4$ just mentioned, and in the property of manganese dioxide of combining with alkalies. If the higher grades of oxidation of manganese are deoxidised in the presence of alkalies, they usually give the dioxide combined with the alkali—for example, in the presence of potash a compound is formed which has the composition $K_2O,5MnO_2$, showing the weak acid character of this oxide. When ignited in the presence of sodium compounds, manganese dioxide frequently forms $Na_2O,8MnO_2$ and $Na_2O,12MnO_2$, and lime when heated with MnO_2 gives from $CaO,8MnO_2$ to $(CaO)_2,MnO_2$ (Rousseau) according to the temperature. Native psilomelane, Mn_3O_5, may be regarded as $MnO,2MnO_2$. Besides which MnO_2 is perhaps a saline compound, MnO,MnO_3 or $(MnO)_3,Mn_2O_7$, and there are reactions which support such a view (Spring, Richards, Traube, and others); for instance, it is known that manganous chloride and potassium permanganate give the dioxide in the presence of alkalies.

Manganese dioxide may be obtained from manganous salts by the action of oxidising agents. If manganous hydroxide or carbonate is shaken up in water through which chlorine is passed, the hypochlorite of the metal is not formed, as is the case with certain other oxides, but manganese dioxide is precipitated: $2MnO_2H_2 + Cl_2 = MnCl_2 + MnO_2,H_2O + H_2O$. Owing to this fact, hypochlorites in the presence of alkalies and acetic acid, when added to a solution of manganous salts, give hydrated manganese dioxide, as was mentioned above. Manganous nitrate also leaves manganese dioxide when heated to 200°. It is also obtained from manganous and manganic salts of the alkalies, when they are decomposed in the presence of a small amount of acid; the practical method of converting the salts MnX_2 into the higher grades of oxidation is given in Chap. XI., note 6.

hydrogen (the oxides of iron give metallic iron under these circumstances), but only to manganous oxide, MnO, shows that manganese is difficult to reduce. A mixture of one of the oxides of manganese with charcoal or organic matter gives fused **metallic manganese** under the powerful heat developed by coke with an artificial draught. The metal was obtained for the first time in this manner by Gahn, after Pott, and more especially Scheele, had in the eighteenth century shown the difference between the compounds of iron and manganese (they were previously regarded as being the same). Manganese is prepared by the same methods as chromium (p. 314), but the purest product is obtained by decomposing Mn_3O_4 with aluminium powder or a strong solution of $MnCl_2$ with sodium amalgam. In the latter case, after the removal of mercury (at about 400°) a powder of manganese is obtained which fuses into a mass with difficulty owing to the ease with which it oxidises. In the first instance a fused metallic mass is obtained direct.[20] Its specific gravity varies between 7·3 and 8·0. It has a light-grey colour with a reddish tint, a feebly metallic lustre, and although it

---

[20] Former chemists often obtained manganese containing carbon. Moissan, by heating the oxides of manganese with carbon in the electric furnace, obtained carbide of manganese, Mn_3C, and remarked that the metal volatilised in the heat of the voltaic arc. Metallic manganese is not prepared on a large scale, nor its alloys with carbon (they readily and rapidly oxidise), but *ferro-manganese* or a coarsely crystalline alloy of iron, manganese, and carbon, which is smelted in blast-furnaces like pig-iron (see Chap. XXII.). This ferro-manganese is employed in the manufacture of steel by Bessemer's and other processes (see Chap. XXII.) and for the manufacture of manganese bronze. However, in America, Green and Wahl (1893) obtained almost pure metallic manganese on a large scale. They first treat the ore of MnO_2 with 30 per cent. sulphuric acid (which extracts all the oxides of iron present in the ore), and then heat it in a reducing flame to convert it into MnO, which they mix with a powder of Al (this is the prototype of Goldschmidt's method), lime and CaF_2 (as a flux), and heat the mixture in a crucible lined with magnesia; a reaction immediately takes place at a certain temperature, and a metal of specific gravity 7·3 is obtained, which contains only a small trace of iron.

Manganese gives two compounds **with nitrogen**, Mn_5N_2 and Mn_3N_2. They were obtained by Prelinger (1894) from the amalgam of manganese, Mn_2Hg_5 (obtained on a mercury anode by the action of an electric current upon a solution of $MnCl_2$); the mercury may be removed from this amalgam by heating it in an atmosphere of hydrogen, and then metallic manganese is obtained as a grey porous mass of specific gravity 7·42. If this amalgam is heated in dry nitrogen, it gives Mn_5N_2 (grey powder, sp. gr. 6·58); but if heated in an atmosphere of NH_3 it gives (as also does Mn_5N_2) Mn_3N_2 (a dark mass with a metallic lustre, sp. gr. 6·21), which, when heated in nitrogen, is converted into Mn_5N_2, and if heated in hydrogen, evolves NH_3 and disengages hydrogen from a solution of NH_4Cl. At all events, manganese is a metal which decomposes water and absorbs oxygen more easily than iron or cobalt. Among the alloys of manganese, besides those with iron, the copper alloys are most important. The alloy, containing 83 per cent. of Cu, 13 of Mn, and 4 of Ni, is called 'manganin' and is used for the wire of resistance batteries, because its electrical conductivity (after it has been repeatedly heated to 120°) varies very slightly within the usual range of temperature. The alloys with Cu, Sn, and Zn (bronzes) are very hard, and their properties can be easily modified at will, so that they are much used in practice.

is very hard, it can be scratched by a file. It rapidly oxidises in air, being converted into a black oxide; water acts on it with the evolution of hydrogen—this decomposition proceeds very rapidly with boiling water, or if the metal contains carbon.

It has been shown above that if manganese dioxide, or any lower oxide of manganese, is heated with an alkali in the presence of air, the mixture absorbs oxygen,[21] and forms an alkaline manganate of a green colour: $2KHO + MnO_2 + O = K_2MnO_4 + H_2O$. Steam is disengaged during the ignition of the mixture, and if this does not take place, there is no absorption of oxygen. The oxidation proceeds much more rapidly if, before igniting in air, potassium chlorate or nitre is added to the mixture, and this is the method of preparing **potassium manganate**, K_2MnO_4. With a small quantity of water the resultant mass gives a dark-green solution, which, when evaporated under the receiver of an air-pump over sulphuric acid, deposits green crystals of exactly the same form as potassium sulphate—namely, six-sided prisms and pyramids. The composition of the product is not changed by being redissolved, if perfectly pure water, free from air and carbonic acid, is taken. But in the presence of even very feeble acids, the solution of this salt changes its colour, becoming red and depositing manganese dioxide. The same decomposition takes place when the salt is heated with water, but when diluted with a large quantity of unboiled water manganese dioxide does not separate, although the solution turns red. This change of colour depends on the fact that potassium manganate, K_2MnO_4, whose solution is green, is transformed into potassium permanganate, $KMnO_4$, whose solution is of a red colour. The reaction proceeding under the influence of acids and a large quantity of water is expressed in the following manner: $3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KHO$. If there is a large proportion of acid and the decomposition is aided by heat, the manganese dioxide and potassium permanganate are also decomposed, with formation of manganous salt. Exactly the same decomposition as takes place under the action of acids is also accomplished by magnesium sulphate, which reacts in many cases like an acid. When water containing atmospheric oxygen in solution acts on a solution of potassium manganate, the oxygen combines directly with the manganate and forms potassium permanganate, without precipitating manganese dioxide, $2K_2MnO_4 + O + H_2O = 2KMnO_4 + 2KHO$. (This reaction is not reversible; see note 22a.) Thus a solution of potassium manganate readily undergoes a very characteristic change in colour; hence this salt received the name of **mineral chameleon.**[22]

[21] Chap. III., note 7.

[22] It was known to the alchemists by this name, but the true explanation of the

Potassium permanganate, $KMnO_4$, crystallises in well-formed long red prisms with a bright-green metallic lustre. In the arts the potash is frequently replaced by soda and by other alkaline bases, but no salt of permanganic acid crystallises so well as the potassium salt, so that this salt is exclusively used in chemical laboratories. One part of the crystalline salt dissolves in 15 parts of water at the ordinary temperature. The solution is of a very deep **red colour**, which is so intense that it is still clearly observable after the liquid has been highly diluted with water. In a solid state it is decomposed by heat, with evolution of oxygen, a residue consisting of the lower oxides of manganese and potassium oxide being left.[22a] A mixture of permanganate of potassium, phosphorus, and sulphur takes fire when struck or rubbed, but a mixture of the permanganate with carbon only takes fire when heated, not when struck. The instability of the salt is also seen from the fact that its solution is decomposed by peroxide of hydrogen, which at the same time it decomposes. A number of substances reduce potassium permanganate to manganese dioxide (in which case the red solution becomes colourless).[23] Many organic substances (although far from all, even when boiled in a solution of permanganate) act in this manner,

---

change in colour is due to the researches of Chevillot, Edwards, Mitscherlich, and Forchhammer. The change in colour of potassium manganate is due to its instability and to its splitting up into two other manganese compounds, a higher and a lower: $3MnO_3 = Mn_2O_7 + MnO_2$. Manganese trioxide is really decomposed in this manner by the action of water (see later): $3MnO_3 + H_2O = 2MnHO_4 + MnO_2$ (Franke, Thorpe, and Humbly). The instability of the salt is proved by the fact of its being deoxidised by organic matter, with the formation of manganese dioxide and alkali, so that a solution of this salt cannot, for instance, be filtered through paper. The presence of an excess of alkali increases the stability of the salt; when heated, it breaks up in the presence of water, with the evolution of oxygen.

The method of preparing **potassium permanganate** will be understood from the above. There are many recipes for preparing this substance, as it and the sodium salt as well are now used in considerable quantities for technical and laboratory purposes. But in all cases the essence of the methods is one and the same. This solution may be boiled, as the liquid will contain free alkali; but the solution cannot be evaporated to dryness, because a strong solution, as well as the solid salt, is decomposed by heat.

By adding a dilute solution of manganous sulphate to a boiling mixture of lead dioxide and dilute nitric acid, the whole of the manganese may be converted into permanganic acid (Crum).

[22a] The solution of this salt with an excess of impure commercial alkali generally acquires a green tint, owing to the formation of a manganous salt, a portion of the oxygen being transferred to the organic matter present in the alkali. Pure solutions of alkalies do not produce this coloration, even after boiling and evaporation.

[23] A solution of potassium permanganate gives a beautiful absorption spectrum (Chap. XIII.). We may here remark that a dilute solution of permanganate of potassium forms a colourless solution with nickel salts, because the green colour of the solutions of nickel salts is complementary to the red. Such a decolorised solution, containing a large proportion of nickel and a small proportion of manganese, decomposes after a time, throws down a precipitate, and re-acquires the green colour proper to the nickel salts.

being oxidised at the expense of a portion of their oxygen. Thus, a solution of sugar decomposes a cold solution of potassium permanganate. In the presence of an excess of alkali, with a small quantity of sugar, the reduction leads to the formation of potassium manganate, $2KMnO_4+2KHO=O+2K_2MnO_4+H_2O$. With a considerable amount of sugar and a more prolonged action, the solution turns brown and precipitates manganese dioxide or even the oxide. In the oxidation of organic bodies by an alkaline solution of $KMnO_4$, three-eighths of the oxygen in the salt are generally utilised for oxidation: $2KMnO_4=K_2O+2MnO_2+O_3$. A portion of the alkali liberated is retained by the manganese dioxide, and the other portion generally combines with the substance oxidised, because the latter most frequently gives an acid with an excess of alkali. A solution of potassium iodide acts in a similar manner, being converted into potassium iodate at the expense of the three atoms of oxygen disengaged by two molecules of potassium permanganate.

In the presence of acids, potassium permanganate acts as an oxidising agent with still greater energy than in the presence of alkalies. At any rate, a greater proportion of oxygen is then available for oxidation, namely, not $\frac{3}{8}$, as in the presence of alkalies, but $\frac{5}{8}$, because in the first instance manganese dioxide is formed, and in the second case manganous oxide, or rather the salt, MnX_2, corresponding with it. Thus, for instance, in the presence of an excess of sulphuric acid, the decomposition is accomplished in the following manner: $2KMnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+3H_2O+5O$. This decomposition, however, does not proceed directly on mixing a solution of the salt with sulphuric acid, and crystals of the salt even dissolve in oil of vitriol without the evolution of oxygen, and this solution only decomposes by degrees after a certain time. This is due to the fact that sulphuric acid liberates free permanganic acid from the permanganate,[24] which acid is stable

---

[24] If sulphuric acid is allowed to act on potassium permanganate without any special precautions, a large amount of oxygen is evolved (it may even explode and inflame), and a violet spray of the decomposing permanganic acid is given off. But if the pure salt (i.e., free from chlorine) is dissolved in pure well-cooled sulphuric acid, without any rise in temperature, a green-coloured liquid settles at the bottom of the vessel. This liquid does not contain any sulphuric acid, and consists of **permanganic anhydride**, Mn_2O_7 (Aschoff, Terreil). It is impossible to prepare any considerable quantity of the anhydride by this method, as it decomposes with explosion as it accumulates, evolving oxygen. Mn_2O_7, in dissolving in sulphuric acid, gives a green solution, which (according to Franke, 1887) contains a compound $Mn_2SO_{10}=(MnO_3)_2SO_4$—that is, sulphuric acid in which both hydrogens are replaced by the group MnO_3, which is combined with OK in permanganate of potassium. This compound with a small quantity of water gives Mn_2O_7; with NaCl in the cold it gives MnO_3Cl (i.e., the chloranhydride of manganic acid), which liquefies in the cold and is very unstable; and when heated to 30°, it gives manganous anhydride or **manganese trioxide**, $(MnO_3)_2SO_4+H_2O=2MnO_3+H_2SO_4+O$. Pure

in solution. But if, in the presence of acids and a permanganate, there is a substance capable of absorbing oxygen—capable, for instance, of passing into a state of higher oxidation—then the reduction of the permanganic acid into manganous oxides sometimes proceeds directly at the ordinary temperature. This reduction is very clearly seen, because the solutions of potassium permanganate are red, whilst the manganous salts are almost colourless. Thus, for instance, nitrous acid and its salts are converted into nitric acid and decolorise the acid solution of the permanganate. Sulphurous anhydride and its salts immediately decolorise potassium permanganate, forming sulphuric acid. Ferrous salts, and, in general, salts of lower grades of oxidation capable of being oxidised in solution, act in exactly the same manner. Sulphuretted hydrogen is also oxidised to sulphuric acid; even mercury is oxidised at the expense of permanganic acid, and decolorises its solution, being converted into mercuric oxide. Moreover, the end point of these reactions may be easily seen, and therefore, having first determined the amount of active oxygen in one volume of a solution of potassium permanganate, and knowing how many volumes are required to effect a given oxidation, it is easy to determine the amount of an oxidisable substance in a

---

manganese trioxide is obtained if the solution of $(MnO_3)_2SO_4$ is poured in drops on to sodium carbonate. Then, together with carbonic anhydride, a spray of manganese trioxide passes over, which may be collected in a well-cooled receiver, and this shows that the reaction proceeds according to the equation: $(MnO_3)_2SO_4 + Na_2CO_3 = Na_2SO_4 + 2MnO_3 + CO_2 + O$ (Thorpe). The trioxide is decomposed by water, forming manganese dioxide and a solution of **permanganic acid**: $3MnO_3 + H_2O = MnO_2 + 2HMnO_4$. The same acid is obtained by dissolving permanganic anhydride in water.

Barium permanganate, $Ba(MnO_4)_2$, when treated with sulphuric acid gives a red solution of the same acid. This barium salt may be prepared by the action of barium chloride on the difficultly soluble silver permanganate, $AgMnO_4$, which is precipitated on mixing a strong solution of the potassium salt with silver nitrate. A solution of permanganic acid deposits manganese dioxide when exposed to the action of light, and also when heated above 60°, and this proceeds the more rapidly the more dilute the solution. Even hydrogen gas is absorbed by a solution of permanganic acid; and charcoal and sulphur are also oxidised by it, as they are by potassium permanganate. Finely divided platinum immediately decomposes permanganic acid. With potassium iodide it liberates iodine (which may afterwards be oxidised into iodic acid). Ammonia is oxidised with evolution of nitrogen. The oxidising action of permanganic acid in a strong solution may be accompanied by flame and the formation of violet fumes of permanganic acid; thus a strong solution of it takes fire when brought into contact with paper, alcohol, alkaline sulphides, fats, &c.

We may add that, according to Franke, 1 part of potassium permanganate with 18 parts of sulphuric acid at 100° gives brown crystals of the salt $Mn_2(SO_4)_3,H_2SO_4,4H_2O$, which yields a precipitate of hydrated manganese dioxide, $H_2MnO_3 = MnO_2,H_2O$, when treated with water.

Spring, by precipitating potassium permanganate with sodium sulphite and washing the precipitate by decantation, obtained a soluble colloidal manganese oxide, whose composition was intermediate between Mn_2O_3 and MnO_2—namely, $Mn_2O_3,4(MnO_2,H_2O)$. MnO and Mn_2O_7 apparently volatilise without decomposition under a low pressure.

solution from the amount of permanganate expended (Marguerite's method).

The oxidising action of $KMnO_4$, like all other chemical reactions, is not accomplished instantaneously, but only gradually. And, as the course of the reaction is here easily followed by determining the amount of salt unchanged in a sample taken at a given moment,[25] the oxidising reaction of potassium permanganate, in an acid liquid, was employed by Harcourt and Esson (1865) as one of the first cases for the investigation of the laws of the **rate of chemical change**,[26] a subject of great importance in chemical mechanics. In their experiments they took oxalic acid, $C_2H_2O_4$, which in oxidising gives carbonic anhydride, whilst, with an excess of sulphuric acid, the potassium permanganate is converted into manganous sulphate, $MnSO_4$, so that the ultimate oxidation will be expressed by the equation: $5C_2H_2O_4+2MnKO_4+3H_2SO_4=10CO_2+K_2SO_4+2MnSO_4+8H_2O$. The influence of the relative amount of sulphuric acid is seen from the annexed table, which gives

---

[25] For rapid and accurate determinations of this kind, advantage is taken of those methods of chemical analysis which are known as 'titrations,' and consist in measuring the volume of solutions of known strength required. Details respecting the theory and practice of titration, in which potassium permanganate is very frequently employed, must be looked for in works on analytical chemistry.

[26] The measurements of velocity and acceleration serve for determining the measure of forces in mechanics, but in that case the velocities are magnitudes of length or paths passed over in a unit of time. The velocity of chemical change embodies a conception of quite another kind. In the first place, the velocities of reactions are magnitudes of the masses which have entered into chemical transformations; in the second place, these velocities can only be relative quantities. Hence the conception of 'velocity' has quite a different meaning in chemistry from that it has in mechanics. Their only common factor is time. If dt be the increment of time and dx the quantity of a substance changed in this space of time, then the fraction (or quotient) dx/dt will express the rate of the reaction. The natural conclusion, arrived at both by Harcourt and Esson, and previously to them (1850) by Wilhelmj (who investigated the rate of conversion, or inversion, of sugar in its passage into dextrose and levulose), is that this velocity is proportional to the quantity of substance still unchanged—i.e., that $dx/dt=C(A-x)$, where C is a constant coefficient of proportionality, and A is the quantity of a substance taken for reaction at the moment when $t=0$ and $x=0$—that is, at the beginning of the experiment, from which the time t and quantity x of substance changed are counted. On integrating the preceding equation, we obtain $\log[A/(A-x)]=kt$, where k is a constant. Hence, knowing A, x, and t, for each reaction, we find k, and it proves to be a constant quantity. Thus, from the figures cited in the text for the reaction: $2KMnO_4+108C_2H_2O_4+14MnSO_4$, it may be calculated that $k=0{\cdot}0114$; for example, $t=44$, $x=68{\cdot}4$ $(A=100)$, whence $kt=0{\cdot}5004$ and $k=0{\cdot}0114$ (see also Chap. XIX., note 3, and Chap. XXII., note 25a).

The researches made by Hood, van't Hoff, Ostwald, Warder, Menschutkin, Konovaloff, and others have a particular significance in this direction. I consider it impossible to enter into the details of this province of theoretical chemistry, although I am quite confident that its development should lead to very important results, especially in respect to chemical equilibria, for van't Hoff has already shown that the limit of reaction in reversible reactions is determined by the attainment of equal velocities for the opposite reactions.

the measure of reaction, p, per 100 parts of potassium permanganate, taken four minutes after mixing, using n molecules of sulphuric acid, H_2SO_4, per $2KMnO_4 + 5C_2H_2O_4$:

$n =$	2	4	6	8	12	16	22
$p =$	22	36	51	63	77	86	92

showing that in a given time (4 minutes) the oxidation is the more perfect the greater the amount of sulphuric acid taken for given amounts of $KMnO_4$ and $C_2H_2O_4$. It is obvious also that the temperature and relative amount of every one of the acting and resulting substances should show their influence on the relative velocity of reaction : thus, for instance, direct experiment showed the influence of the admixture of manganous sulphate. When a large proportion of oxalic acid (108 molecules) was taken to a large mass of water and to 2 molecules of permanganate 14 molecules of manganous sulphate were added, the quantity, x, of the potassium permanganate acted on (in percentages of the potassium permanganate taken) in t minutes (at 16°) was as follows:

$t=$	2	5	8	11	14	44	47	53	61	68
$x=$	5·2	12·1	18·7	25·1	31·3	68·4	71·7	75·8	79·8	83·0

The same phenomena are observed in every case which has been investigated, and this branch of theoretical or physical chemistry, now studied by many, promises to explain the course of chemical transformations from a fresh point of view, which is closely allied to the doctrine of affinity, because the rate of reaction is without doubt connected with the magnitude of the affinities acting between the reacting substances.

CHAPTER XXII

IRON, COBALT, AND NICKEL

JUDGING from the atomic weights, and the forms of the higher oxides of the elements already considered, it is easy to form an idea of the seven groups of the periodic system. Such are, for instance, the typical series Li, Be, B, C, N, O, F, or the third series, Na, Mg, Al, Si, P, S, Cl. The seven usual types of higher oxides from R_2O to R_2O_7 correspond with them (Chap. XV.). The position of the eighth group is quite separate, and is determined by the fact that, as we have already seen, in each group of metals having a greater atomic weight than potassium, a distinction ought to be made between the elements of the even and those of the uneven series. The series of even elements, commencind with a strikingly alkaline element (potassium, rubidium, cæsium), together with the uneven series following it, and concluding with a haloid (bromine, iodine), forms a large period, the properties of whose members repeat themselves in other similar periods. The elements of the eighth group are situated between the elements of the even series and the elements of the uneven series following them in these larger periods (see Preface). The properties of the elements belonging to group VIII., in many respects independent and striking, are shown with typical clearness in the case of iron, which resembles manganese in many respects, and is the well-known representative of this group.

Iron is one of those elements which are widely diffused, not only in the crust of the earth, but also throughout the entire universe. Its oxides and other compounds are found in the most diverse portions of the earth's crust; but iron is not found on the earth's surface in a free state, because it easily oxidises under the action of air. It is occasionally found in the native state in meteorites, or aërolites, which fall upon the earth.

Meteoric iron is formed outside the earth.[1] Meteorites are fragments which are carried round the sun in orbits, and fall upon the earth

---

[1] The composition of meteoric iron is variable. It generally contains nickel, phosphorus, carbon, &c. The schreibersite of meteoric stones contains Fe_4Ni_2P.

when coming into proximity with it during their motion in space. The meteoric dust, on passing through the upper parts of the atmosphere, and becoming incandescent from friction with the gases, produces that phenomenon which is familiar under the name of 'falling stars.'[2] Such

[2] Comets and the rings of Saturn ought now to be considered as consisting of an accumulation of such meteoric cosmic solid particles or bodies. Perhaps the part played by these minute bodies scattered throughout space is much more important in the formation of the largest celestial bodies than has hitherto been imagined. The investigation of this branch of astronomy, due to Schiaparelli, and begun in the last decades of the nineteenth century, has a bearing on the whole of natural science.

The question arises as to why the iron in meteorites is in a free state, whilst on the earth it is in a state of combination. Does not this tend to show that the condition of our globe is very different from that of the rest? My answer to this question has been already given in Vol. I., Chap. VIII., note 57. It is my opinion that inside the earth there is a mass similar in composition to meteorites—that is, containing rocky matter and metallic iron, partly carburetted. In conclusion, I consider it will not be out of place to add the following explanations. According to the theory of the distribution of pressures (see my treatise *On Barometric Levelling*, 1876, p. 48 *et seq.*) in an atmosphere of mixed gases, it follows that two gases, whose densities are d and d_1, and whose relative quantities or partial pressures at a certain distance from the centre of gravity are h and h_1, will, when at a greater distance from the centre of attraction, present a different ratio of their masses $x : x_1$—that is, of their partial pressures—which may be found by the equation $d_1(\log h - \log x) = d(\log h_1 - \log x_1)$. If, for instance, $d : d_1 = 2 : 1$, and $h = h_1$ (that is to say, the masses are equal at the lower height) $= 1000$, then when $x = 10$ the magnitude of x_1 will not be 10 (i.e., the mass of a gas at a higher level whose density is 1 will not be equal to the mass of a gas whose density is 2, as was the case at a lower level), but much greater—namely, $x_1 = 100$—that is, the lighter gas will predominate over a heavier one at a higher level. Therefore, when the whole mass of the earth was in a state of vapour, the substances having a greater vapour density (speaking relatively, for instance, to a unit of mass of oxygen) accumulated about the centre and those with a lesser vapour density at the surface. And as the vapour densities depend on the atomic and molecular weights, those substances which have small atomic and molecular weights ought to have accumulated at the surface, and those with high atomic and molecular weights, which are the least volatile and the easiest to condense, at the centre. Thus it becomes apparent why such light elements as hydrogen, carbon, nitrogen, oxygen, sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, and their compounds predominate at the surface and largely form the earth's crust. There is also now much iron in the sun, as spectrum analysis shows, and therefore it must have entered into the composition of the earth and other planets, but would have accumulated at the centre, because the density of its vapour is certainly large and it easily condenses. There was also oxygen near the centre of the earth, but not sufficient to combine with the iron. The former, as a much lighter element, accumulated principally at the surface, where we at the present time find all oxidised compounds and even a remnant of free oxygen. This gives the possibility not only of explaining, in accordance with cosmogonic theories, the predominance of oxygen compounds on the surface of the earth, with the occurrence of unoxidised iron in the interior of the earth and in meteorites, but also of understanding why the density of the whole earth (over 5) is far greater than that of the rocks (1 to 3) composing its crust. And if all the preceding arguments and theories be true, it must be admitted that the interior of the earth and other planets contains metallic (unoxidised) iron, which, however, is only found on the surface as aërolites. And then, assuming that aërolites are the fragments of planets which have crumbled to pieces, as it were, during cooling (this has been held to be the case by astronomers, judging from the paths of aërolites), it is readily understood why they should be composed of metallic iron, and this would explain its occurrence in is the doctrine concerning meteorites, and the fact of their containing rocky (silicious) matter and metallic iron shows, therefore, that outside the earth the elements and their aggregation are in some degree the same as upon the earth itself.

The most widely diffused terrestrial compound of iron is iron bisulphide, FeS_2, or **iron pyrites.** It occurs in formations of both aqueous and igneous origin, and sometimes in enormous masses. It is a substance having a greyish-yellow colour, with a metallic lustre, and a specific gravity of 5·0; it crystallises in the regular system.[2a]

The oxides are the principal ores used for producing metallic iron. The majority of the ores contain ferric oxide, Fe_2O_3, either in a free state or combined with water, or else in combination with ferrous oxide, FeO. **Ferric oxide** in a separate form appears sometimes as crystals of the rhombohedral system, having a metallic lustre and greyish steel colour; they are brittle, and form a red powder, and have a specific gravity of about 5·25. In type of oxidation and properties ferric oxide resembles alumina; it is, however, although with difficulty, soluble in acids, even when anhydrous. The crystalline oxide bears the name of **specular iron ore,** but ferric oxide most often occurs in a non-crystalline form in masses having a red fracture, and is then known as **red hæmatite.** In this form, however, it is rather a rare ore, and is principally found in veins. The hydrates of ferric oxide, **ferric hydroxides,**[3] are most often found in aqueous or stratified formations,

---

the depths of the earth, which we assumed as the basis of our theory of the formation of naphtha (Chap. VIII., notes 57–60). Grains of metallic iron have been found disseminated in certain basalts or volcanic rocks on the surface of the earth, and may have proceeded from iron in the interior of the earth.

[2a] Immense deposits of iron pyrites are known in various parts of Russia. On the river Msta, near Borovitsi, thousands of tons are yearly collected from the detritus of the neighbouring rocks. In the governments of Toula, Riazan, and in the Donetz district continuous layers of pyrites occur among the coal seams. Very thick beds of pyrites are also known in many parts of the Caucasus. But the deposits of the Urals are particularly vast, and have been worked for a long time. Amongst these I shall indicate only the deposits on the Soymensky estate, near the Kishteimsky Works; the Kaletinsky deposits, near the Virhny-Isetsky Works (containing 1–2 per cent. Cu); on the banks of the river Koushaivi, near Koushvi (3–5 per cent. Cu); and the deposits near the Bogoslovsky Works (3–5 per cent. Cu). Iron pyrites (especially that containing copper which is extracted after roasting) is now chiefly employed for roasting, as a source of SO_2 for the manufacture of sulphuric acid; but the remaining oxide of iron is perfectly suitable for smelting into pig iron, although it gives a sulphurous pig iron (the sulphur may be easily removed by subsequent treatment, especially with the aid of ferro-manganese in Bessemer's process). The great technical importance of iron pyrites leads to its sometimes being imported from great distances; for instance, into England from Spain. Besides which, when heated in closed retorts, FeS_2 gives sulphur, and, if allowed to oxidise in damp air, green vitriol, $FeSO_4$.

[3] The hydrated ferric oxide is found in nature in a dual form. It is somewhat rarely met with in the form of a crystalline mineral called **gothite,** whose specific gravity is 4·4 and composition $Fe_2H_2O_4$, or $FeHO_2$, or Fe_2O_3,H_2O; it is most frequently found

and are known as **brown hæmatites**; they generally have a brown colour, form a yellowish-brown powder, and have no metallic lustre, but an earthy appearance. They dissolve easily in acids and diffuse through other formations, especially clays (for instance, ochre); they sometimes occur in reniform and similar masses, evidently of aqueous origin. Such are, for instance, the so-called *bog* or *lake* and *peat* ores found at the bottom of marshes and lakes, and also under and in peat beds. This ore is formed from water containing ferrous carbonate in solution, which, after absorbing oxygen, deposits ferric hydroxide. In rivers and springs, iron is found as ferrous carbonate, held in solution, like $CaCO_3$, through the agency of carbonic acid; hence the existence of chalybeate springs containing $FeCO_3$. This ferrous carbonate, or **siderite**, is either found as a non-crystalline product of evidently aqueous origin, or as a crystalline spar called **spathic iron ore**. The reniform deposits of the former are most remarkable; they are called spherosiderites, and sometimes form whole strata in the Jurassic and Carboniferous formations. **Magnetic iron ore**, $Fe_3O_4 = FeO,Fe_2O_3$, in virtue of its purity and practical uses, is a very important ore; it is a compound of ferrous and ferric oxides, is naturally magnetic, has a specific gravity of 5·1, crystallises in well-formed crystals of the regular system, is with difficulty soluble in acids, and sometimes forms enormous masses, as, for instance, Mount Blagodat in the Central Urals, and Mount Magnitni in the Southern Urals. However, in most cases—for instance, at Korsak-Mogila (to the north of Berdiansk and Nogaiska, near the Sea of Azov), or at Krivoi Rog (to the west of Ekaterinoslav)—the magnetic iron ore is mixed with other iron ores. In the Urals, the Caucasus (without mentioning Siberia), and in the district adjoining the basin of the Don, Russia possesses the richest iron ores in the world. To the south of Moscow, in the governments of Toula and Nijni-novgorod, in the Olonetz district, and in the government of Orloffsky (near Zinovieff in the district of Kromsky), and in many other places, there are likewise abundant supplies of iron ores amongst the deposited aqueous formations; the siderite of Orloffsky, for instance, is distinguished by its great purity.[4]

as brown ironstone, forming a dense mass of fibrous reniform deposits of the composition $2Fe_2O_3,3H_2O$. In bog ore and other similar ores we most often find a mixture of this hydrated ferric oxide with clay and other impurities.

[4] The ores of iron, like many other minerals, are worked by means of vertical, horizontal, or inclined shafts which reach and penetrate the veins and strata containing the ore deposits. The mass of ore excavated is raised to the surface, then sorted, and subjected to roasting and other treatment. In every case the ore contains foreign matter. In the extraction of iron, which is the cheapest metal, the dressing of an ore is in most cases unprofitable, and only ores rich in metal are worked—namely, those containing at least 20 per cent. It is often profitable to transport very rich and pure ores

Iron is also found in the form of various other compounds—for instance, in certain silicates, and also in some phosphates—but these forms are comparatively rare in nature in a pure state, and have not the industrial importance of those natural compounds of iron previously mentioned. In small quantities iron enters into the composition of every kind of **soil** and of all rocky formations. As ferrous oxide, FeO, is isomorphous with magnesia, and ferric oxide, Fe_2O_3, with alumina, isomorphous substitution is here possible, and hence minerals are not infrequently found in which the quantity of iron varies considerably; such, for instance, are pyroxene, amphibole, certain varieties of mica, &c. Although much iron oxide is deleterious to the growth of vegetation, still plants do not flourish without iron; it enters as an indispensable component into the composition of all **organisms**; in the ash of plants we always find more or less of its compounds. It also occurs in blood, and forms one of the colouring matters in it; 100 parts of the blood of the highest organisms contain about 0·05 of iron.

The **reduction** of the ores of iron into metallic iron is in principle very simple, because when the oxides of iron are strongly heated with charcoal, hydrogen, carbonic oxide, and other reducing agents,[5]

(with as much as 70 per cent. of iron) from long distances. The details concerning the working and extraction of metals will be found in special treatises on metallurgy and mining.

[5] The reduction of iron oxides by hydrogen belongs to the order of reversible reactions, and is therefore determined by a limit which is here expressed by the attainment of the same pressure as in the case where hydrogen acts on iron oxides, and as in the case where (at the same temperature) water is decomposed by metallic iron. The calculations referring to this matter were made by Henri Sainte-Claire Deville (1870). Spongy iron was placed in a tube having a temperature t, one end of which was connected with a vessel containing water at 0° (vapour pressure = 4·6 mm.) and the other end with a mercury pump and pressure gauge which determined the limiting pressure, p, attained by the dry hydrogen (subtracting the pressure of the water vapour from the pressure observed). A tube was then taken containing an excess of iron oxide. It was filled with hydrogen, and the pressure p_1 of the residual hydrogen observed when the water was condensed at 0°.

t = 200°	440°	860°	1040°
p = 95·9	25·8	12·8	9·2 mm.
p_1 = —	—	12·8	9·4 mm.

The equality of the pressure of the hydrogen in the two cases is evident.

By taking ferric oxide, Fe_2O_3, Moissan observed that at 850° it passed into magnetic oxide, Fe_3O_4; at 500°, into ferrous oxide, FeO; and at 600°, into metallic iron. Wright and Luff (1878) found that (*a*) the temperature of reaction depends on the condition of the oxide taken; for instance, precipitated ferric oxide is reduced by hydrogen at 85°, that obtained by oxidising the metal or from its nitrate at 175°; (*b*) when other conditions are the same, the reduction by carbonic oxide commences earlier than that by hydrogen, and the reduction by hydrogen still earlier than that by charcoal; (*c*) the reduction is effected with greater facility when a greater quantity of heat is evolved during the reaction. Ferric oxide obtained by heating ferrous sulphate to a red heat begins to be reduced by carbonic oxide at 202°, by hydrogen at 260°, by charcoal at 480°, whilst for magnetic oxide, Fe_3O_4, the temperatures are 200°, 290°, and 450° respectively.

they easily give metallic iron. But the matter is rendered more difficult by the fact that the iron does not melt at the heat developed by the combustion of the charcoal, and therefore it does not separate from those mechanically mixed impurities which are found in the iron ore. This is obviated by the following very remarkable property of iron: at a high temperature it is capable of combining with a small quantity (from 2 to 5 per cent.) of carbon, and then forms **cast iron,** which easily **melts** in the heat developed by the combustion of charcoal in air. For this reason metallic iron is not obtained directly from the ore, but is only formed after the further treatment of the cast iron, the first product extracted from the ore being cast iron containing carbide of iron.[5a] The fused mass of cast iron disposes itself in the furnace below the slag—that is, the impurities of the ore fused by the heat of the furnace. If these impurities did not fuse they would block up the furnace in which the ore was being smelted, and the continuous smelting of the cast iron would not be possible;[6] it would be necessary periodically to cool the furnace and heat it up again, which means a wasteful expenditure of fuel, and hence in the production of cast iron the object in view is to obtain all the earthy impurities of the ore in the shape of a fused mass or slag. Only in rare cases does the ore itself form a mass which fuses at the temperature employed, and these cases are objectionable if much iron oxide is carried away in the slag. The impurities of the ores most often consist of certain mixtures—for instance, a mixture of clay and sand, or a mixture of limestone and clay, or quartz, &c. These impurities do not separate of themselves, or do not fuse. The difficulty of the industry lies in forming an easily fusible slag, into which the whole of the foreign matter of the ore would pass and flow down to the

---

[5a] With iron, carbon most easily and frequently forms a carbide having the composition Fe_3C (6·7 per cent. of C). Abel first extracted it from steel, and Moissan showed that it is formed directly in the electric furnace by saturating iron with carbon. When this alloy, or cast iron saturated with carbon, is formed and the heating of the mass prolonged, a moment occurs when it becomes so viscid that it cannot be poured from the crucible. If it is then rapidly cooled in water (Chap. VIII., note 17a), it gives a uniform crystalline mass of carbide of sp. gr. 7·07, which readily rusts in air; its powder burns in oxygen (see note 9). Crystals of carbide embedded in steel are called 'cementite.'

[6] The primitive methods of iron manufacture were conducted by intermittent processes in hearths resembling smith's fires. As evidenced by the uninterrupted action of the steam boiler, or the process of lime burning, and the continuous preparation and condensation of sulphuric acid or the uninterrupted smelting of iron, every industrial process becomes increasingly profitable and complete under the condition of the continuous action, as far as possible, of all agencies concerned in the production. This method lessens the cost of labour, simplifies the supervision of the work, renders the product uniform, and frequently introduces a very great economy in the expenditure of fuel and at the same time presents the simplicity and perfection of an equilibrated system. Hence every manufacturing operation should be a continuous one.

bottom of the furnace above the heavier cast iron. This is effected by mixing certain **fluxes** with the ore and charcoal. A flux is a substance which, when mixed with the foreign matter of the ore, forms a fusible vitreous mass or slag. The flux used for silica is limestone with clay; for limestone a definite quantity of silica is used, the best procedure having been arrived at by experiment and by long practice in iron smelting and other metallurgical processes.[7]

Thus the following materials have to be introduced into the furnace where the smelting of the iron ore is carried on: (1) the iron ore, composed of oxide of iron and foreign matter; (2) the flux required to form a fusible slag with the foreign matter; (3) the carbon which is necessary (*a*) for reducing, (*b*) for combining with the reduced iron to form cast iron, (*c*) principally for the purpose of combustion and the heat generated thereby, necessary not only for reducing the iron and transforming it into cast iron, but also for melting the slag, as well as the cast iron—and (4) the air necessary for the combustion of the charcoal. The air is introduced after a preparatory heating in order to economise fuel and to obtain the highest temperature. The air is forced in under pressure by means of a special blast arrangement. This permits of an exact regulation of the heat and rate of smelting. All these component parts necessary for the smelting of iron must be contained in a vertical, that is, **shaft furnace**, which at the base must have a receptacle for the accumulation of the slag and cast iron formed, in order that the operation may proceed without interruption. The walls of such a furnace ought to be built of fire-proof materials if it be designed to serve for the continuous production of cast iron by charging the ore, fuel, and flux into the mouth of the furnace, forcing a blast of air into the lower part, and running out the molten iron and slag from

---

[7] The composition of slag suitable for iron smelting most often approaches the following: 50 to 60 per cent. SiO_2, 5 to 20 Al_2O_3, the rest of the mass consisting of MgO, CaO, MnO, FeO. Thus the most fusible slag (according to the observations of Bodeman) contains the alloy $Al_2O_3,4CaO,7SiO_2$. On altering the quantity of magnesia and lime, and especially of the alkalies (which increases the fusibility) and of silica (which decreases it), the temperature of fusion changes with the relation between the total quantity of oxygen and that in the silica. Slags of the composition RO,SiO_2 are easily fusible, have a vitreous appearance, and are very common. Basic slags approach the composition $2RO,SiO_2$. Hence, knowing the composition and quantity of the foreign matter in the ore, it is at once easy to find the quantity and quality of the flux which must be added to form a suitable slag. The smelting of iron is rendered more complex by the fact that the silica, SiO_2, which enters into the slag and fluxes is capable of forming a slag with the iron oxides. In order that the least quantity of iron may pass into the slag, it is necessary for it to be reduced before the temperature is attained at which the slags are formed (about 1000°), which is effected by reducing the iron, not with charcoal itself, but with carbonic oxide. From this it will be understood how the progress of the whole treatment may be judged by the properties of the slags. Details of this complicated and well-studied subject will be found in works on metallurgy.

below. The whole operation is conducted in furnaces known as **blast furnaces.**[8] The annexed illustrations, figs. 103 and 104 (the latter taken

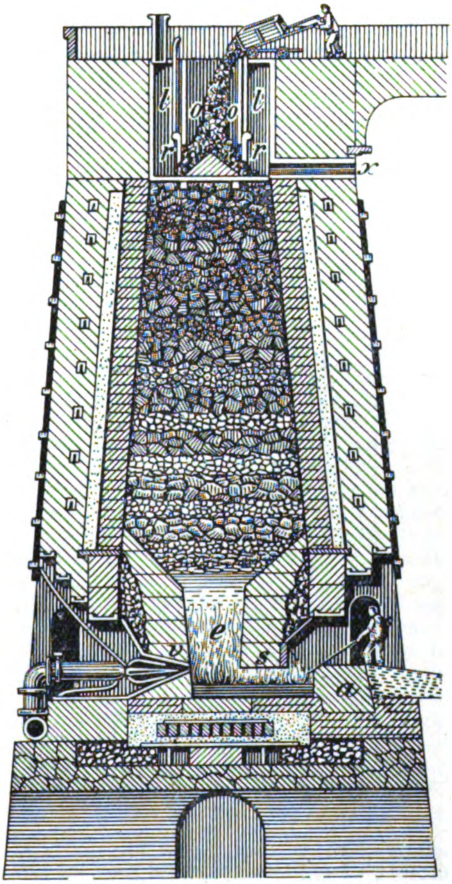


FIG. 103.—Vertical section of blast furnace. Scale 1 : 200. *x* is the pipe by which the furnace gases are drawn off. On the cylinder, *o o*, which does not reach the cone below it, another cylinder, *r r*, moves by means of the rods *l l*; *r r* is kept pushed down except when the furnace is being charged, when it is raised. *e* shows the hearth of the furnace, and *v* one of the *tuyères* through which the hot blast is introduced. Between *s* and *a* is an opening for letting the molten cast iron and slag run out.

[8] The section of a blast furnace is represented by two truncated cones joined at their bases, the upper cone being longer than the lower one; the lower cone is terminated by the hearth, or almost cylindrical cavity in which the cast iron and slag collect, one side being provided with apertures for drawing off the iron and slag. The air is blown into the blast furnace through special pipes situated over the hearth, as shown in the sections. The air previously passes through a series of cast-iron pipes, heated by the combustion of the carbonic oxide obtained from the upper parts of the furnace, where it is formed as in a 'gas-producer.' The amount of combustible blast furnace gases

by kind permission from Thorpe's 'Dictionary of Applied Chemistry') represent vertical sections of such furnaces. These furnaces are generally

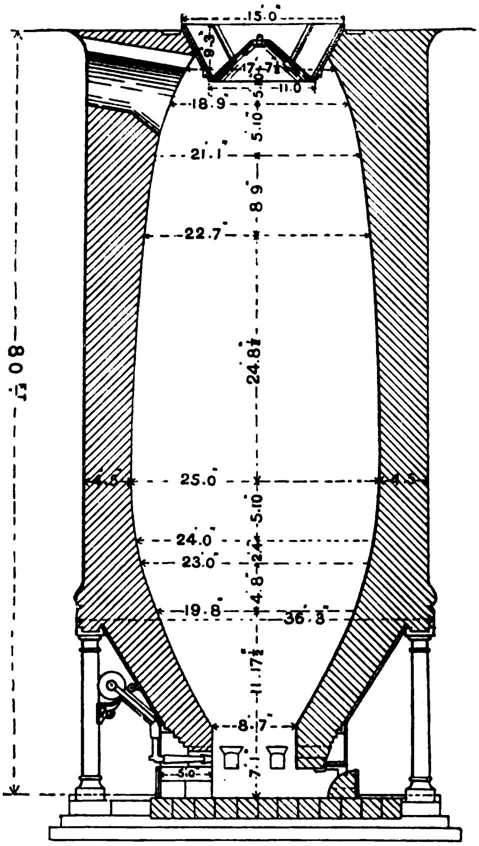


FIG. 104.—Vertical section of a modern Cleveland blast furnace capable of producing 300 to 1,000 tons of pig iron weekly. The outer casing is of riveted iron plates, the furnace being lined with refractory fire-brick. It is closed at the top by a 'cap and cone' arrangement, by means of which the charge can be fed into the furnace at suitable intervals by lowering the movable cone.

containing CO is so large that they not only suffice for heating the blast, but also for gas-engines. The blast furnace acts continuously until it is worn out; the iron is tapped off twice a day, and the furnace allowed to cool a little from time to time, so as not to be spoilt by the increasing heat, and to enable it to withstand long usage.

Blast furnaces worked with charcoal fuel are not so high, and in general give a smaller yield than those using coke, because the latter are worked with heavier charges than the former. Coke furnaces yield 20,000 tons and over of pig iron a year. In the United States there are blast furnaces 30 metres high, and upwards of 600 cubic metres capacity, yielding as much as 130,000 tons of pig iron, requiring a blast of about 750 cubic metres of air per minute, heated to 600°, and consuming about 0·85 part of coke per 1 part of pig iron produced. At the present time the world produces as much as 40,000,000 tons of pig iron a year, about $\frac{9}{10}$ of which is converted into wrought iron of large dimensions, varying from fifty to ninety feet in height. They are sometimes built against rising ground in order to afford easy access to the top where the ore, flux, and charcoal or coke are charged.[8a]

The **cast iron** formed in blast furnaces is not always of the same quality. When slowly cooled it is soft, has a grey colour, and is not

---

and steel. The chief producers are the United States (about 15 million tons a year) and England (about 9 million tons a year); Russia yields about 2½ million tons a year. About a million tons of pyrites are produced by the world in a year.

[8a] In order to more thoroughly grasp the chemical process which takes place in blast furnaces, it is necessary to follow the course of the material charged in at the top and that of the air passing through the furnace. From 50 to 200 parts of carbon are expended on 100 parts of iron. The ore, flux, and coke are charged into the top of the furnace, in layers, as the cast iron formed in the lower parts flows down to the bottom and so causes the whole contents of the furnace to subside, thus forming an empty space at the top, which is again filled up with the afore-mentioned mixture. During its downward course this mixture is subjected to increasing heat. This rise of temperature first drives off the moisture of the ore mixture and then leads to the formation of the products of the dry distillation of coal or charcoal. Little by little the subsiding mass attains a temperature at which the heated carbon reacts with the carbonic anhydride passing upwards through the furnace and transforms it into carbonic oxide. This is the reason why carbonic anhydride is not evolved from the furnace, but chiefly carbonic oxide. As regards the ore itself, on being heated to about 600° to 800° it is reduced at the expense of the **carbonic oxide** and not by carbon itself (see note 5); thus, $Fe_2O_3 + 3CO = Fe_2 + 3CO_2$. The reduced iron, on further subsidence and contact with carbon, forms cast iron, which flows to the bottom of the furnace. In these lower layers, where the temperature is highest (about 1300°), the foreign matter of the ore finally forms slag, which is also fusible, with the aid of fluxes. The air blown in from below, through the so-called *tuyères*, encounters carbon in the lower layers of the furnace, and burns it, converting it into carbonic anhydride. It is evident that this develops the highest temperature in these lower layers of the furnace, because here the combustion of the carbon is effected by heated air. The carbonic acid formed rises higher, encounters incandescent carbon, and forms with it carbonic oxide. This heated carbonic oxide acts as a reducing agent on the iron ore, and is reconverted by it into carbonic anhydride; this gas meets with more carbon, and again forms carbonic oxide, which again acts as a reducing agent. The final transformation of the carbonic anhydride into carbonic oxide is effected in those parts of the furnace where the reduction of the oxides of iron does not take place, but where the temperature is still high enough to reduce the carbonic anhydride. The ascending mixture of carbonic oxide and nitrogen, CO_2, &c., is then withdrawn through special lateral apertures formed in the upper cold parts of the furnace walls, and is conducted through pipes to the furnaces used for heating the air, and also to other furnaces used for the further processes of iron manufacture, and even (since the close of the nineteenth century) to gas engines. The fuel of blast furnaces consists of wood charcoal (this is the most expensive material, but the pig iron produced is the purest, because charcoal does not contain any sulphur, while coke does), anthracite (for instance, in Pennsylvania, and in Russia at Pastouhoff's works in the Don district), coke, coal, and even wood and peat. It must be borne in mind that the utilisation of naphtha and naphtha refuse would probably give very profitable results in metallurgical processes.

The process just described is accompanied by a series of other processes. Thus, for instance, in the blast furnace a considerable quantity of cyanogen compounds is formed. This takes place because the nitrogen of the air blast comes into contact with incandescent carbon and various alkaline matters contained in the foreign matter of the ores.

completely soluble in acids. When treated with acids a residue of graphite remains ; it is known as **grey** or soft cast iron. This is the general form of the ordinary cast iron used for casting various objects, because in this state it is not so brittle as in the shape of **white cast iron**, which does not leave particles of graphite when dissolved, but yields its carbon in the form of hydrocarbons. This white cast iron is characterised by its whitish-grey colour, dull lustre, the crystalline structure of its fracture (more homogeneous than that of grey iron), and such hardness that a file will hardly cut it. When white cast iron is produced (from manganese ore) at high temperatures (and with an excess of lime), and contains little sulphur and silica but a considerable amount of carbon (as much as 5 per cent.), it acquires a coarse crystalline structure which increases in proportion to the amount of manganese, and it is then known under the name of 'spiegeleisen' (and 'ferromanganese').[9]

Cast iron is a material which is suitable either for direct application for casting in moulds or for working up into **wrought iron** and **steel.** The latter principally differ from cast iron in their containing less carbon—thus, steel contains from 1 to 0·5 per cent. of carbon and far less silicon and manganese than cast iron; wrought iron does not generally contain more than 0·25 per cent. of carbon and not more than 0·25 per cent. of the other impurities. Thus the essence of the work-

---

[9] The specific gravity of white cast iron is about 7·5, and that of grey cast iron, 7·0. Grey cast iron generally contains less manganese and more silica than white, but both contain from 2 to 3 per cent. of carbon. The difference between the varieties of cast iron depends on the condition of the carbon which enters into the composition of the iron. In white cast iron the carbon is in combination with the iron, as the compound CFe_3 (note 5). Abel and Osmond and others extracted this compound, which is sometimes called 'carbide,' from tempered steel, which stands to unannealed steel as white cast iron does to grey. In any case the compound of the iron and carbon in white cast iron is chemically very unstable, because when slowly cooled it decomposes, with separation of graphite, just as a solution when slowly cooled yields a portion of the substance dissolved. The separation of carbon in the form of graphite on the conversion of white cast iron into grey is never complete, however slowly the separation be carried on; part of the carbon remains in combination with the iron in the same state in which it exists in white cast iron. Hence when grey cast iron is treated with acids, the whole of the carbon does not remain in the form of graphite, but a part of it is separated as hydrocarbons. It is sufficient to re-melt grey cast iron and cool it quickly to re-transform it into white cast iron. It is not carbon alone that influences the properties of cast iron; when it contains a considerable amount of sulphur, cast iron remains white, even after having been slowly cooled. The same is observed in cast iron very rich in manganese (5 to 7 per cent.), and in this latter case the fracture is very distinctly crystalline and brilliant When cast iron contains a large amount of manganese, the quantity of carbon may also be increased. Grey cast iron not having a uniform structure is much more liable to various changes than dense and more uniform white cast iron. White cast iron is used not only for conversion into wrought iron and steel, but also in those cases where great hardness is required, although it be accompanied by a certain brittleness, for instance, for making rollers, ploughshares, &c.

ing-up of cast iron into steel and wrought iron consists in the removal of the greater part of the carbon and other elements, S, P, Mn, Si, &c. This is effected by means of oxidation, because the oxygen of the atmosphere, oxidising the iron at a high temperature, forms with it solid oxides; and the latter, coming into contact with the carbon contained in the cast iron, are deoxidised, forming wrought iron and carbonic oxide, which is evolved from the mass in a gaseous form. It is evident that the oxidation must be carried on with a molten mass in a state of agitation, so that the oxygen of the air may be brought into contact with the whole mass of carbon contained in the cast iron, or else the operation is effected by means of the addition of oxygen compounds of iron (oxides, ores, as in Martin's process). Cast iron melts much more easily than wrought iron and steel, and therefore, as the carbon separates, the mass in the furnace (in puddling) or hearth (in the bloomery process) becomes more and more solid; moreover, the degree of hardness forms, to a certain extent, a measure of the amount of carbon separated, and the operation may terminate in the formation of either steel or wrought iron.[10] In any case, the iron used for

---

[10] This direct process of separating the carbon from cast iron is termed **puddling.** It is conducted in reverberatory furnaces. The cast iron is placed on the bed of the furnace and melted; through a special aperture, the puddler stirs up the oxidising mass of cast iron, pressing the oxides into the molten iron. This resembles kneading dough, and the process introduced into England became known as puddling. It is evident that the puddled mass, or bloom, is a heterogeneous substance obtained by mixing, and hence one part of the mass will still be rich in carbon, another will be poor, some parts will contain oxide not reduced, &c. The further treatment of the puddled mass consists in hammering and drawing it out into flat pieces, which on being hammered become more homogeneous, and when several pieces are welded together and again hammered out a still more homogeneous mass is obtained. The quality of the steel and iron thus formed depends principally on their uniformity. In order to obtain a more homogeneous metal for manufacturing articles out of steel, it is drawn into thin rods, which are tied together in bundles and then again hammered out. As an example of what may be attained in this direction, imitation Damascus steel may be cited; it consists of twisted and plaited wire, which is then hammered into a dense mass. (Real damascened wootz steel may be made by melting a mixture of the best iron with graphite ($\frac{1}{12}$) and iron rust; the article is then corroded with acid, and the carbon remains in the form of a pattern.)

Steel and wrought iron are manufactured from cast iron by puddling. They were formerly obtained by the **bloomery process,** carried out in a fire similar to a blacksmith's forge, fed with charcoal and provided with a blast; a pig of cast iron is gradually pushed into the fire, and portions of it melt and fall to the bottom of the hearth, coming into contact with an air blast, and are thus oxidised. The bloom thus formed is then squeezed and hammered. It is evident that this process is only available when the charcoal used in the fire does not contain any foreign matter which might injure the quality of the iron or steel—for instance, sulphur or phosphorus. Only wood charcoal may be used with impunity, from which it follows that this process can only be carried on where the manufacture of iron can be conducted with this fuel. Coal and coke contain the above-mentioned impurities, and would therefore produce iron of a brittle nature, and thus it would be necessary to have recourse to puddling, the fuel being burnt on a special hearth, separate from the cast iron, whereby the impurities of the fuel do not come into industrial purposes contains impurities. **Chemically pure iron** may be obtained by precipitating iron from a solution (a mixture of ferrous

---

contact with it. The manufacture of steel from cast iron may also be conducted in fires; but, in addition to this, it is also now prepared by many other methods. One of the long-known processes is called **cementation,** by which steel is prepared from wrought iron but not from cast iron. For this process strips of iron are heated to redness for a considerable time while immersed in powdered charcoal; during this operation the iron at the surface combines with the charcoal, which, however, does not penetrate; after this the iron strips are re-forged, drawn out again, and cemented anew, this process being repeated until a steel of the desired quality is formed—that is, containing the requisite proportion of carbon. The **Bessemer** process occupies the front rank among the newer methods (since 1855); it is so called from the name of its inventor. This process consists in running melted cast iron into converters (holding about 6 tons of cast iron)—that is, egg-shaped receivers, fig. 105, capable of revolving on trunnions (in order to charge in the cast iron and discharge the steel), and forcing a stream of air through small apertures at a considerable pressure. Combustion of the iron and carbon (Mn, &c.) at a high temperature then takes place, resulting from the bubbles of oxygen thus penetrating the mass of the cast iron. The carbon, however, burns to a greater extent than the iron, and a mass is therefore obtained which is much poorer in carbon than cast iron. As the combustion proceeds rapidly, the temperature rises to such an extent that even the wrought iron which may be formed remains in a molten condition, whilst the steel, being more fusible than the wrought iron, remains very liquid. In half an hour the mass is ready. The purest possible cast iron is used in the Bessemer process, because sulphur and phosphorus do not burn out like carbon, silicon, and manganese.

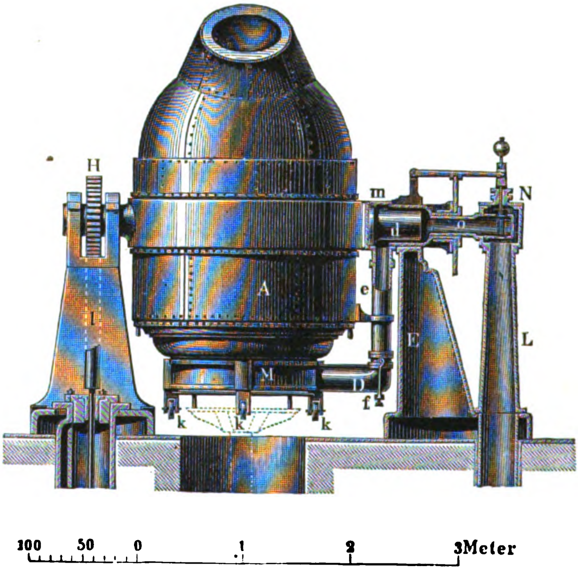


FIG. 105.—Bessemer converter, constructed of iron plate and lined with ganister. The air is carried by the tubes, L, O, D, to the bottom, M, from which it passes by a number of holes into the converter. The converter is rotated on the trunnion *d* by means of the rack and pinion H, when it is required either to receive molten cast iron from the melting furnaces or to pour out the steel.

sulphate with magnesium sulphate or ammonium chloride) by the prolonged action of a feeble galvanic current; the iron may be then

The presence of manganese enables the sulphur to be removed with the slag, and the presence of lime or magnesia, which are introduced into the lining of the converter, facilitates the removal of the phosphorus. This basic Bessemer process, or **Thomas-Gilchrist process**, introduced about 1880, enables ores containing a considerable amount of phosphorus, which had hitherto only been used for cast iron, to be used for making wrought iron and steel. Naturally the greatest uniformity will be obtained by re-melting the metal. Steel is re-melted, in small wind furnaces, in masses not exceeding 30 kilos; a liquid metal is formed, which may be cast in moulds. A mixture of wrought and cast iron is often used for making cast steel (the addition of a small amount of metallic Al improves the homogeneity of the castings by facilitating the passage of the impurities into slag). Large steel castings are made by simultaneous fusion in several furnaces and crucibles; in this way, castings up to 80 tons or more, such as large ordnance, may be made. This molten, and therefore homogeneous, steel is called **cast steel**. In the last quarter of the nineteenth century **Martin's process** for the manufacture of steel has come largely into use; it was invented in France about 1860, and with the use of regenerative furnaces it enables large quantities of cast steel to be made at a time. It is based on the melting of cast iron with iron oxides and iron itself—for instance, pure ores, scrap, &c. There the carbon of the cast iron and the oxygen of the oxide form carbonic oxide, and the carbon therefore burns out, and thus cast steel is obtained from cast iron, providing, naturally, that there is a requisite proportion and corresponding degree of heat. The advantage of this process is that not only do the carbon, silicon, and manganese, but also a great part of the sulphur and phosphorus of the cast iron burn out at the expense of the oxygen of the iron oxides. The manufacture of steel and its applications for rails, armour plate, guns, boilers, &c., have developed to an enormous extent, thanks to the invention of cheap processes for the manufacture of large masses of homogeneous cast steel. Wrought iron may also be melted, but the heat of a blast furnace is insufficient for this. It melts easily in the oxyhydrogen flame and in the regenerator furnace (Chap. IX., note 22). It may be obtained in a molten state directly from cast iron, if the latter be melted with nitre and sufficiently stirred up. Considerable oxidation then takes place inside the mass of cast iron, and the temperature rises to such an extent that the wrought iron formed remains liquid. Iron may also be obtained direct in a fused state by burning a mixture of Fe_2O_3 and aluminium powder (thermite, Chap. III., note 42). A method is also known for obtaining wrought iron directly from rich iron ores by the action of carbonic oxide; the wrought iron is then formed as a spongy mass (which forms an excellent filter for purifying water), and may be worked up into wrought iron or steel either by forging or by dissolving in molten cast iron.

Everybody is more or less familiar with the **difference in the properties of steel and wrought iron**. Iron is remarkable for its softness, pliability, and small elasticity, whilst steel may be characterised by its capability of attaining elasticity and hardness if it be cooled suddenly after having been heated to a definite temperature, or, as it is termed, *tempered*. But if tempered steel be re-heated and slowly cooled, it becomes as soft as wrought iron, and can then be cut with the file and forged, and in general can be made to assume any shape, like wrought iron. In this soft condition it is called *annealed steel*. The transition from tempered to annealed steel thus takes place in a similar way to the transition from white to grey cast iron. Steel, when homogeneous, has considerable lustre, and such a fine granular structure that it takes a very high polish. Its fracture clearly shows the granular nature of its structure. The possibility of tempering steel enables it to be used for making all kinds of cutting instruments, because annealed steel can be forged, turned, drawn (under rollers, for instance, for making rails, bars, &c.), filed, &c., and it may then be tempered, ground, and polished. The method and temperature of tempering and annealing steel determine its hardness and other qualities. Steel is generally tempered to the required degree of hardness in the following manner: It is first strongly heated (for instance, up to 600°) and then plunged into water—that obtained as a dense mass. This method (Böttcher and Klein) gives, as R. Lenz showed, iron containing occluded hydrogen, which is disengaged on heating, after which it becomes soft. If pure ferric hydroxide, which is easily prepared by the precipitation of solutions of ferric salts by means of ammonia, be heated in a stream of hydrogen, it forms, first of all, a dull-black powder which takes fire in air (pyrophoric

---

is, hardened by rapid cooling (it then becomes as brittle as glass). It is then heated until the surface assumes a certain colour, and finally cooled either quickly or slowly. When steel is heated up to 220°, its surface acquires a yellow colour (surgical instruments): it first of all becomes straw-coloured (razors, &c.), and then gold-coloured; then at a temperature of 250° it becomes brown (scissors), then red, then light blue at 285° (springs), indigo at 300° (files), and finally sea-green at about 340°. These colours are only the tints of thin films, like the hues of soap bubbles, and appear on the steel because a thin layer of oxides is formed over its surface. Steel rusts more slowly than wrought iron, and is more soluble in acids than cast iron, but less so than wrought iron. Its specific gravity is about 7·6 to 7·9.

The formation and structure of steel, the effect of different impurities on it, and its variation under different circumstances now form one of the best investigated portions of metallurgy, and this would not be the place to discuss it. I shall only remark that now, when fused iron is obtained in the Siemens furnace or converter with as much ease as steel, the distinction between iron and steel (for the cast or fused metal) has lost its former sense and significance, although it should be still retained in speaking of the metal which has not been subjected to fusion. And as the properties of the metal (generally called steel) vary in dependence upon the amount of carbon in it, I give the following classification, due to Cockerell (1878): (1) *Very mild steel* contains from 0·05 to 0·20 per cent. of carbon, breaks with a weight of 40 to 50 kilos per square millimetre, and has an extension of 20 to 30 per cent.; it may be welded, like wrought iron, but cannot be tempered; it is used in sheets for boilers, armour plate and bridges, nails, rivets, &c., as a substitute for wrought iron; (2) *mild steel*, from 0·20 to 0·35 per cent. of carbon; resistance to tension 50 to 60 kilos, extension 15 to 20 per cent., not easily welded, and tempers badly; used for axles, rails, and railway tyres, for cannons and guns, and for parts of machines destined to resist bending and torsion; (3) *hard steel*, carbon 0·35 to 0·50 per cent., breaking weight 60 to 70 kilos per square millimetre, extension 10 to 15 per cent., cannot be welded, takes a temper; used for rails, all kinds of springs, swords, parts of machinery in motion subjected to friction, spindles of looms, hammers, spades, hoes, &c.; (4) *very hard steel*, carbon 0·5 to 0·65 per cent., tensile breaking weight 70 to 80 kilos, extension 5 to 10 per cent., does not weld, but tempers easily; used for small springs, saws, files, knives, and similar instruments.

The variations in the properties of iron and steel depend on the impurities which they contain. In general, the iron used in the arts still contains carbon and always a certain quantity of silicon, manganese, sulphur, phosphorus, &c. A variety in the proportion of these component parts changes the quality of the iron. In addition to this the change which soft wrought iron, having a fibrous structure, undergoes when subjected to repeated blows and vibrations is considerable; it then becomes granular and brittle. This explains to a certain degree the want of stability of some iron objects—such as truck axles, which must be renewed after a certain term of service, as otherwise they become brittle. It is evident that there are innumerable intermediate transitions from wrought iron to steel and cast iron.

I may add that the Urals, Donetz district, and the Kusnetz coal-fields of Western Siberia offer the greatest advantages for the development of a vast iron industry, because these localities not only contain enormous supplies of excellent iron ore, but also coal, which is necessary for smelting it. The Ural district with its cheap charcoal is best suited for the production of the higher grades of steel, as is shown in my work, *The Iron Industry of the Urals in* 1899, written after my journey to the Urals.

iron) and then a grey powder of pure iron which does not burn in the air. The powdery substance first obtained is an iron suboxide; when thrown into the air it ignites, forming the oxide Fe_3O_4. If a small quantity of the pure powdery iron be fused in the oxyhydrogen flame (with an excess of oxygen) in a piece of lime and mixed with powdered glass, pure molten iron will be formed, because in the oxyhydrogen flame iron melts and burns, but the substances mixed with the iron oxidise first. Pure iron has a silvery white colour and a specific gravity of 7·84 ; it melts at a temperature higher than the melting-points of silver, gold, nickel, and steel, viz., about 1400°—1500° and below the melting-point of platinum (1750°).[11] But pure iron becomes soft at a temperature considerably below that at which it melts, and may then be easily forged, welded, and rolled or drawn into sheets and wire.[11a] Pure iron may be rolled into an exceedingly thin sheet, weighing less than a sheet of ordinary paper of the same size. This ductility is the most important property of iron in all its forms, and is most marked with sheet iron, and least so with cast iron, whose ductility, compared with that of wrought iron, is small.[12]

---

[11] According to information supplied by A. T. Skinder's experiments at the Oboukoff Steel Works, 140 volumes of liquid molten steel give 128 volumes of solid metal. By means of a galvanic current of great intensity and using dense charcoal as one electrode and iron as the other, Bernadoss welded iron and fused holes through sheet iron. Soft wrought iron, like steel and soft malleable cast iron, may be easily melted in Siemens's regenerative furnaces, and in furnaces heated with naphtha.

[11a] Gore (1869), Tait, Barret, Tchernoff, Osmond, and others observed that at a temperature approaching 600°—that is, between dark and bright-red heat—all kinds of wrought iron undergo a peculiar change called **recalescence**, i.e., a spontaneous rise of temperature. If iron be considerably heated and allowed to cool, it may be observed that at this temperature the cooling stops—that is, latent heat is disengaged, corresponding with a change in condition. The specific heat, electrical conductivity, magnetic and other properties then also change. In tempering, and also in annealing, &c., the temperature of recalescence must not be reached. It is evident that a change of the internal condition is here encountered, exactly similar to the transition from a solid to a liquid, although there is no evident physical change.

[12] The particles of steel are linked together or connected more closely than those of the other metals; this is shown by the fact that it only **breaks** with a tensile stress of 50–80 kilos per sq. mm., whilst wrought iron only withstands about 30 kilos, cast iron 10, copper 35, silver 23, platinum 30, and wood 8. The elasticity of iron, steel, and other metals is expressed by the so-called **coefficient of elasticity**. Let a rod be taken whose length is L; if a weight, P, be hung from the extremity of it, it will lengthen by l The less it lengthens under other equal conditions, the more elastic the material, if it resumes its original length when the weight is removed. It has been shown by experiment that the increase in length, l, due to elasticity, is directly proportional to the length L and the weight P, and inversely proportional to the area of cross-section, but changes with the material. The coefficient of elasticity expresses that weight (in kilos per sq. mm.) under which a rod having a cross section taken as 1 (we take 1 sq. mm.) acquires double the length by tension. Naturally in practice materials do not withstand such a lengthening, but under a certain weight they attain a limit of elasticity, i.e., they stretch permanently (undergo deformation). Neglecting fractions (as the elasticity of metals

The chemical properties of iron have been already repeatedly mentioned in preceding chapters. Iron **rusts** in air at the ordinary temperature—that is to say, it becomes covered with a layer of iron oxides. Here, without doubt, the moisture of the air plays a part, because in dry air iron does not oxidise at all, and also because, more particularly, ammonia is always found in iron rust ; the ammonia must arise from the action of the hydrogen of the water, at the moment of its separation, on the nitrogen of the air. Highly polished steel does not rust nearly so readily, but if moistened with water, it easily becomes coated with rust. As rust depends on the access of moisture, iron may be preserved from rust by coating it with substances which prevent the moisture coming into contact with it. Thus arises the practice of covering iron objects with paraffin,[13] varnish, oil, paints, or enamelling it with a glassy-looking flux possessing the same coefficient of expansion as iron, or with a dense scoria (formed by the heat of superheated steam), or with a compact coating of various metals. Wrought iron (both as sheet iron and in other forms), cast iron, and steel are often coated with tin, copper, lead, nickel, and similar metals, which prevent contact with the air. These metals preserve iron very effectually from rust if they form a perfectly compact surface ; but in those places where the iron becomes exposed, either accidentally or from wear, rust appears much more quickly than on a uniform iron surface, because towards these metals (and also towards the rust) the iron will then behave as an electro-positive pole in a galvanic couple, and will hence attract oxygen. A coating of zinc does not produce this inconvenience, because iron is electro-negative with reference to zinc, in consequence of which galvanised iron does not easily rust, and even an iron boiler containing lumps of zinc rusts less than one without zinc.[14] Iron oxidises at a high temperature, forming **iron scale,** Fe_3O_4, composed of ferrous and ferric oxides, and, as has been seen, decomposes water and acids with the evolution of hydrogen. It is also capable of decomposing salts and oxides of other metals, which property is applied in the arts

---

varies not only with the temperature, but also with forging, purity, &c.), the coefficient of elasticity is for steel and iron 20,000; for copper and brass 10,000; for silver 7,000; for glass 6,000; for lead 2,000; and for wood 1,200.

[13] Paraffin is one of the best preservatives for iron against oxidation in the air. I found this by experiments about 1860, and immediately published the fact. This method is now very generally applied.

[14] See Chapter XVIII., note 34a. Based on the rapid oxidation of iron and its increase in volume in the presence of water and salts of ammonium, a packing is used for water mains and steam pipes which is tightly hammered into the socket-joints. This packing consists of a mixture of iron filings and a small quantity of sal-ammoniac (and sulphur) moistened with water; after a certain lapse of time, especially after the pipes have been used, this mass swells to such an extent that it hermetically seals the joints of the pipes.

for the extraction of copper, silver, lead, tin, &c. For this reason iron is soluble in the solutions of many salts—for instance, in cupric sulphate, with precipitation of copper and formation of ferrous sulphate.[15] When iron **acts on acids** it always **forms compounds**, FeX_2—that is, corresponding to the suboxide FeO—answering to magnesium compounds, and hence two atoms of hydrogen are replaced by one of iron. Strongly oxidising acids, like nitric acid, may transform the ferrous salt which is forming, into the higher degree of oxidation or the ferric salt (corresponding with the sesquioxide, Fe_2O_3), but this is a secondary reaction. Iron, although easily soluble in dilute nitric acid, loses this property when plunged into strong fuming nitric acid; after this operation it even loses the property of solubility in other acids until the external coating formed by the action of the strong nitric acid is mechanically removed. This condition of iron is termed the passive state. **The passive condition** of iron depends on the formation, on its surface, of a coating of oxide, due to the iron being acted on by the lower oxides of nitrogen contained in the fuming nitric acid.[16] Strong nitric acid which does not contain these lower oxides, does not render iron passive, but it is only necessary to add some alcohol or other reducing agent which forms these lower oxides in the nitric acid, and the iron will assume the passive state.

Iron readily combines with non-metals—for instance, with chlorine, iodine, bromine, sulphur, and even with phosphorus and carbon—and with metals, although it fuses with difficulty. Mn, Cr, W, Cu, and other metals combine with and dissolve in Fe, and in so doing modify its properties. On the other hand Fe greatly alters the properties of Cu, Al, &c., when dissolved in them, although no definite compounds of them are known, owing to the difficulties presented by their investigation. Mercury, which acts on most metals, does not act directly on iron, and the **iron amalgam**, or solution of iron in mercury, which is used for electrical machines, is only obtained in a particular way—namely, with the co-operation of a sodium amalgam, in which the iron

---

[15] Here, however, a ferric salt may also be formed (when all the iron has dissolved and the cupric salt is still in excess), because the cupric salts are reduced by ferrous salts. Cast iron is also dissolved.

[16] Powdery reduced iron is passive with regard to nitric acid of a specific gravity of 1·87, but when heated the acid acts on it. This passiveness disappears in the magnetic field. Saint-Edme attributes the passiveness of iron (and nickel) to the formation of nitride of iron on the surface of the metal, because he observed that when heated in dry hydrogen, ammonia is evolved by passive iron.

Remsen observed that if a strip of iron is immersed in acid and placed in the magnetic field, it is dissolved principally at its middle part—that is, the acid acts more feebly at the poles. According to Étard (1891), strong nitric acid dissolves iron in making it passive, although the action is a very slow one.

dissolves and by means of which it is reduced from solutions of its salts.

When iron acts on acids it forms ferrous salts of the type FeX_2, and in the presence of air and oxidising agents these change by degrees into ferric salts of the type FeX_3. The faculty of passing from the ferrous to the ferric state is particularly developed in ferrous hydroxide. If sodium hydroxide is added to a solution of ferrous sulphate or green vitriol, $FeSO_4$,[17] a white precipitate of **ferrous hydroxide,** $Fe(OH)_2$, is obtained; but on exposure to the air, even under water, it turns green, becomes grey, and finally brown, owing to the oxidation which it undergoes. Ferrous hydroxide is very sparingly soluble in water; its solution has, however, a distinct alkaline reaction, which is due to its being a fairly energetic basic oxide. In any case, ferrous oxide is far more energetic than ferric oxide, so that if ammonia be added to a solution containing a mixture of a ferrous and a ferric salt, at first ferric hydroxide only will be precipitated. If barium carbonate, $BaCO_3$, is shaken up in the cold with ferrous salts, it does not precipitate them—that is, does not change them into ferrous carbonate; but it completely

---

[17] **Iron vitriol** or **green vitriol,** sulphate of iron or ferrous sulphate, generally crystallises from solutions, like magnesium sulphate, with seven molecules of water, $FeSO_4,7H_2O$. This salt is not only formed by the action of iron on sulphuric acid, but also by the action of moisture and air on iron pyrites, especially when these are previously roasted ($FeS_2 + O_2 = FeS + SO_2$), and in this condition it easily absorbs the oxygen of damp air ($FeS + O_4 = FeSO_4$). Green vitriol is obtained in many processes as a by-product. Like all the ferrous salts, it has a pale-greenish colour, hardly perceptible in solution. If it be desired to preserve it without change—that is, so as not to contain ferric compounds—it is necessary to keep it hermetically sealed. This is best done by expelling the air by means of sulphurous anhydride; the SO_2 removes oxygen from any ferric compounds which might be formed, and is itself changed into sulphuric acid, so that the oxidation of the ferrous compound does not take place in its presence. Unless these precautions are taken, green vitriol turns brown, changing partly into the ferric salt. When turned brown, it is not completely soluble in water, because during its oxidation a certain amount of free insoluble ferric oxide is formed: $6FeSO_4 + O_3 = 2Fe_2(SO_4)_3 + Fe_2C_2$. In order to cleanse such mixed green vitriol from the oxide, it is necessary to add some sulphuric acid and iron and boil the mixture; the ferric salt is then transformed into the ferrous state: $Fe_2(SO_4)_3 + Fe = 3FeSO_4$.

Green vitriol is used for the manufacture of Nordhausen sulphuric acid (Chap. XX.), for preparing ferric oxide, in many dye works (for preparing the indigo vats and reducing blue indigo to white), and in many other processes; it is also a very good disinfectant, and is the cheapest salt from which other compounds of iron may be obtained.

The other ferrous salts (excepting the yellow prussiate, which will be mentioned later) are but little used, and it is therefore unnecessary to dwell upon them. We shall only mention **ferrous chloride,** which, in the crystalline state, has the composition $FeCl_2,4H_2O$. It is easily prepared; for instance, by the action of hydrochloric acid on iron, and in the anhydrous state by the action of hydrochloric acid gas on metallic iron at a red heat. The anhydrous ferrous chloride then volatilises in the form of colourless cubic crystals. Ferrous oxalate (or the double potassium salt) acts as a powerful reducing agent, and is frequently employed in photography (as a developer).

separates all the iron from ferric salts in the cold, according to the equation : $Fe_2Cl_6 + 3BaCO_3 + 3H_2O = Fe_2O_3,3H_2O + 3BaCl_2 + 3CO_2$. If ferrous hydroxide is boiled with a solution of potash, the water is decomposed, hydrogen is evolved, and the ferrous hydroxide oxidised. The ferrous salts are in all respects similar to those of magnesium and zinc ; they are isomorphous with them, but differ from them in that the ferrous hydroxide is not soluble either in aqueous potash or ammonia. In the presence of an excess of ammonium salts, however, a certain proportion of the iron is not precipitated by alkalies and alkali carbonates, which fact points to the formation of double ammonium salts.[18] The ferrous salts have a dull **greenish** colour, and form solutions also of a pale-green colour, whilst the ferric salts have a **brown** or reddish-brown colour. The ferrous salts, being capable of oxidation, form active reducing agents—for instance, under their action gold chloride, $AuCl_3$, deposits metallic gold, nitric acid is transformed into lower oxides, and the higher oxides of manganese also pass into the lower forms of oxidation. All these reactions take place with especial ease in the presence of an excess of acid. This depends on the fact that the ferrous oxide, FeO (or salt), acting as a reducing agent, turns into ferric oxide, Fe_2O_3 (or salt), and in the ferric state requires more acid for the formation of a normal salt than in the ferrous condition. Thus, in the normal ferrous sulphate, $FeSO_4$, there is one equivalent of iron to one equivalent of sulphur (in the sulphuric radicle) but in the neutral ferric salt, $Fe_2(SO_4)_3$, there is one equivalent of iron to one and a half of sulphur in the form of the elements of sulphuric acid.[19]

---

[18] Ferrous sulphate, like magnesium sulphate, readily forms double salts—for instance, $(NH_4)_2SO_4,FeSO_4,6H_2O$. This salt does not oxidise in air so rapidly as green vitriol and is therefore used for standardising $KMnO_4$ solutions.

[19] The transformation of ferrous oxide into ferric oxide is not completely effected in air, as then only a part of the suboxide is converted into ferric oxide. Under these circumstances the so-called **magnetic oxide** of iron is generally produced, which contains molecular proportions of the suboxide and oxide—namely, $FeO,Fe_2O_3 = Fe_3O_4$. This substance, as already mentioned, is found in nature and in iron scale. It is also formed when most ferrous and ferric salts are heated in air ; thus, for instance, when ferrous carbonate, $FeCO_3$ (either native or as the precipitate given by soda in a solution of FeX_2), is heated it loses the elements of carbonic anhydride, and magnetic oxide remains. This oxide of iron is attracted by a magnet, and is on this account called magnetic oxide, although it does not always show magnetic properties. If magnetic oxide is dissolved in any acid—for instance, hydrochloric—which does not act as an oxidising agent, a ferrous salt is first formed and ferric oxide remains, which is also capable of passing into solution. The best way of preparing the hydrate of the magnetic oxide is by decomposing a mixture of ferrous and ferric salts with ammonia ; it is, however, indispensable to pour this mixture into the ammonia, and not *vice versa*, as in that case the ferrous oxide would at first be precipitated alone, and then the ferric oxide. The compound thus formed has a bright-green colour, and when dried forms a black powder. Other combinations of ferrous with ferric oxide are known, as also are compounds of ferric oxide

The most simple oxidising agent for transforming ferrous into ferric salts is chlorine in the presence of water—for instance, $2FeCl_2+Cl_2=Fe_2Cl_6$, or generally, $2FeO+Cl_2+H_2O=Fe_2O_3+2HCl$. When such a transformation is required, it is best to add to the ferrous solution, potassium chlorate and hydrochloric acid; chlorine is formed by their mutual reaction and acts as an oxidising agent. Nitric acid produces a similar effect, although more slowly. Ferrous salts may be completely and rapidly oxidised into ferric salts by means of chromic acid or permanganic acid, $HMnO_4$, in the presence of acids—for example, $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$. This reaction is easily observed by the change of colour, and its termination is easily seen, because potassium permanganate forms solutions of a bright-red colour, and when added to a solution of a ferrous salt the above reaction immediately takes place *in the presence of acid*, and the solution then becomes colourless, because all the substances formed are only faintly coloured in solution. Directly all the ferrous compound has passed into the ferric state, any excess of permanganate which is added communicates a red colour to the liquid (see Chap. XXI.).

Thus, when ferrous salts, FeX_2, are acted on by oxidising agents, they pass into the ferric form, FeX_3, whilst under the action of reducing agents the reverse reaction occurs. Sulphuretted hydrogen may, for instance, be used for this complete transformation, for under its influence ferric salts are reduced with separation of sulphur—for example, $Fe_2Cl_6+H_2S=2FeCl_2+2HCl+S$. Sodium thiosulphate acts in a similar way: $Fe_2Cl_6+Na_2S_2O_3+H_2O=2FeCl_2+Na_2SO_4+2HCl+S$. Metallic iron or zinc,[20] in the presence of acids, or sodium amalgam, &c., acts like hydrogen, and has also a similar reducing action, and this furnishes the best method for reducing ferric salts to ferrous salts—for instance, Fe_2Cl_6

---

with other bases. Thus, for instance, compounds are known containing 4 molecules of ferrous oxide to 1 of ferric oxide. These are also magnetic, and are formed by heating iron in air. The magnesia compound, MgO,Fe_2O_3, is prepared by passing gaseous hydrochloric acid over a heated mixture of magnesia and ferric oxide. Crystalline magnesium oxide is then formed, and black shiny octahedral crystals of the above-mentioned composition. This compound is analogous to the aluminates—for instance, to spinel. Bernheim (1888) and Rousseau (1891) obtained many similar compounds of ferric oxide, and their composition apparently corresponds with that of the hydrates (note 22) known for the oxide.

[20] Copper and cuprous salts also reduce ferric oxide to ferrous oxide, and are themselves turned into cupric salts. The essence of the reactions is expressed by the following equations: $Fe_2O_3+Cu_2O=2FeO+2CuO$; $Fe_2O_3+Cu=2FeO+CuO$. This fact is made use of in analysing copper compounds, the quantity of copper being ascertained by the amount of ferrous salt obtained. An excess of ferric salt is required to complete the reaction. Here we have an example of reverse reaction; the ferrous oxide or its salt in the presence of alkali transforms the cupric oxide into cuprous oxide and metallic copper, as was observed by Lovel, Knopp, and others.

$+Zn=2FeCl_2+ZnCl_2$. Thus **the transition from ferrous salts to ferric salts, or vice versa, is always possible.**[21]

Ferric oxide, or sesquioxide of iron, Fe_2O_3, is found in nature, and is artificially prepared in the form of a red powder by many methods. Thus, after heating green vitriol, a red oxide of iron remains, called **colcothar,** which is used as an oil paint, principally for painting wood. The same substance in the form of a very fine powder (rouge) is used for polishing glass, steel, and other objects. If a mixture of ferrous sulphate with an excess of common salt be strongly heated, crystalline ferric oxide will be formed, having a dark-violet colour, and resembling certain natural varieties of this substance. When iron pyrites is heated for preparing sulphurous anhydride, ferric oxide also remains behind; it is used as a pigment. On the addition of an alkali to a solution of a ferric salt, a brown precipitate of ferric hydroxide is formed, which when heated (even when boiled in water, that is, at about 100°, according to Tomassi) easily parts with the water, and leaves red anhydrous ferric oxide. Pure ferric oxide does not show any magnetic properties, but when heated to a white heat it loses oxygen and is converted into the magnetic oxide. Anhydrous ferric oxide which has been heated to a high temperature is with difficulty soluble in acids (but it is soluble when heated in strong acids, and also when fused with potassium hydrogen sulphate), whilst ferric hydroxide, at all events that which is precipitated from salts by means of alkalies, is very readily soluble in acids. The precipitated **ferric hydroxide** has the composition $2Fe_2O_3, 3H_2O$, or $Fe_4H_6O_9$. If this ordinary hydroxide is rendered anhydrous (by heating), at a certain moment it becomes incandescent—that is, it loses a certain quantity of heat. This self-incandescence depends on internal displacement produced by the transition of the easily soluble (in acids) variety into the difficultly soluble variety, and does not

---

[21] We shall here mention the reactions by means of which it may be ascertained whether the ferrous compound has been entirely converted into a ferric compound, or *vice versa*. There are two substances which are best employed for this purpose: potassium ferricyanide, $FeK_3C_6N_6$, and potassium thiocyanate, KCNS. The first of these gives with ferrous salts a blue precipitate of an insoluble salt, having a composition $Fe_5C_{12}N_{12}$; but with ferric salts it does not form any precipitate, and only gives a brown colour, and therefore when transforming a ferrous salt into a ferric salt, the completion of the transformation may be detected by taking a drop of the liquid on paper or on a porcelain plate and adding a drop of the ferricyanide solution. If a blue precipitate is formed, part of the ferrous salt still remains; if there is none, the transformation is complete. The thiocyanate does not give any marked coloration with ferrous salts; but with ferric salts in the most dilute state it forms a bright-red soluble compound, and therefore, when transforming a ferric salt into a ferrous salt, we must proceed as before, testing a drop of the solution with thiocyanate, when the absence of a red colour will prove the total transformation of the ferric salt into the ferrous state, and if a red colour appears it shows that the transformation is not yet complete.

depend on the loss of water, since the anhydrous oxide undergoes the same change. In addition to this there exists a ferric hydroxide, or hydrated oxide of iron, which, like the strongly heated anhydrous iron oxide, is difficultly soluble in acids. On losing water, or after the loss of water, this hydroxide does not undergo such self-incandescence, because no such internal displacement (loss of energy or heat) occurs with it as that which is peculiar to the ordinary oxide of iron. The ferric hydroxide which is difficultly soluble in acids has the composition Fe_2O_3,H_2O. This hydroxide is obtained by prolonged ebullition of water in which ferric hydroxide, prepared by the oxidation of ferrous oxide, is suspended, and also sometimes by similar treatment of the ordinary hydroxide, after it has been for a long time in contact with water. The transition of one hydroxide to another is apparent by a change of colour; the easily soluble hydroxide is redder, and the sparingly soluble hydroxide more yellow in colour.[22]

The normal salts of the composition Fe_2X_6 or FeX_3 correspond with ferric oxide—for example, the exceedingly volatile **ferric chloride,** Fe_2Cl_6, which is easily prepared in the anhydrous state by the action of chlorine on heated iron.[23] Such also is the normal **ferric nitrate,**

---

[22] The **two ferric hydroxides** are characterised not only by the above-mentioned properties, but also by the fact that with potassium ferrocyanide, $K_4FeC_6N_6$, the first hydroxide immediately gives a blue colour depending on the formation of Prussian blue, whilst the second hydroxide does not give any reaction whatever with this salt. The first hydroxide is entirely soluble in nitric, hydrochloric, and all other acids; whilst the second sometimes (not always) forms a brick-coloured liquid, which appears turbid and does not give the reactions peculiar to the ferric salts (Péan de Saint-Gilles, Scheurer-Kestner). In addition to this, when the smallest quantity of an alkaline salt is added to this liquid, ferric oxide is precipitated. Thus, a colloidal solution is formed (hydrosol), which is exactly similar to the hydrosol of silica (Chap. XVII.), according to which example the hydrosol of ferric oxide may be obtained.

If ordinary ferric hydroxide is dissolved in acetic acid, a solution of the colour of red wine is obtained, which has all the reactions characteristic of ferric salts. But if this solution (formed in the cold) is heated to the boiling-point, its colour is very rapidly intensified, a smell of acetic acid becomes apparent, and the solution then contains a new variety of ferric oxide. If the boiling of the solution is continued, acetic acid is evolved, and the modified ferric oxide is precipitated. If the evaporation of the acetic acid is prevented (in a closed or sealed vessel), and the liquid heated for some time, the whole of the ferric hydroxide passes into the insoluble form, and if some alkaline salt be added (to the hydrosol formed), the whole of the ferric oxide will then be precipitated in its insoluble form.

All the phenomena observed respecting ferric oxide (colloidal properties, various forms, formation of double basic salts) demonstrate that this substance, like silica, alumina, Cr_2O_3, lead hydroxide, &c., is polymerised, and that the composition is represented by $(Fe_2O_3)_n$.

[23] The ferric compound which is most used in practice (for instance, in medicine, for cauterising, stopping bleeding, &c.—Oleum Martis) is **ferric chloride,** Fe_2Cl_6, easily obtainable by dissolving the ordinary hydrated oxide of iron in hydrochloric acid. It is obtained in the anhydrous state by the action of chlorine on heated iron. The experiment is carried on in a porcelain tube, and a solid **volatile substance** is then formed in

$Fe_2(NO_3)_6$; it is obtained by dissolving iron in an excess of nitric acid,

the shape of brilliant violet scales which very readily absorb moisture from the air, and when heated with water decompose into crystalline ferric oxide and hydrochloric acid: $Fe_2Cl_6 + 3H_2O = 6HCl + Fe_2O_3$. Ferric chloride is so volatile that the density of its vapour may be determined. At 440° this has the value 164·0 referred to hydrogen; the formula Fe_2Cl_6 corresponds with a density of 162·5. An aqueous solution of this salt has a brown colour. On evaporating and cooling the solution, crystals separate containing 6 or 12 molecules of H_2O, so that the solution then probably contains, not Fe_2Cl_6, but $Fe_2(OH)_6,6HCl$, although this cannot be stated with certainty. Ferric chloride is soluble not only in water, but also in alcohol (similarly to magnesium chloride, &c.) and in ether. If the latter solutions are exposed to the rays of the sun, they become colourless, and deposit ferrous chloride, $FeCl_2$, chlorine being disengaged. After a certain lapse of time, the aqueous solutions of ferric chloride decompose with precipitation of a basic salt, thus demonstrating the instability of ferric chloride, like the other salts of ferric oxide (note 22). This salt is much more stable in the form of double salts, like all the ferric salts, and also the salts of many other feeble bases. Potassium (or ammonium) chloride forms with it very beautiful red crystals of a double salt, having the composition $Fe_2Cl_6,4KCl,2H_2O$. When a solution of this salt is evaporated it decomposes, with separation of potassium chloride.

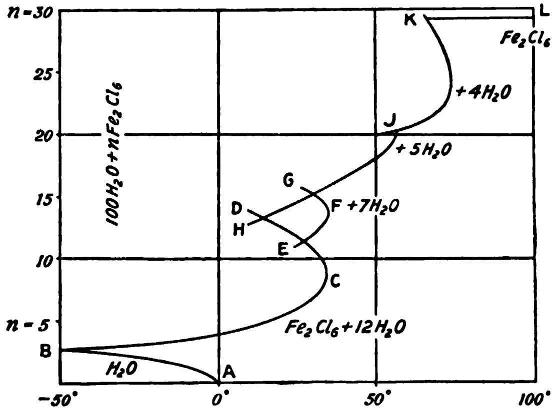


FIG. 106.—Diagram of the solubility of Fe_2Cl_6.

B. Roozeboom (1892) studied in detail (as for $CaCl_2$, Chap. XIV., note 50) the separation of different hydrates from saturated solutions of Fe_2Cl_6 at various concentrations and temperatures; he found that there are 4 crystallohydrates, with 12, 7, 5, and 4 molecules of water respectively. An orange-yellow only slightly hygroscopic hydrate, $Fe_2Cl_6,12H_2O$, is most easily and usually obtained and melts at 37°; its solubility at different temperatures is represented by the curve BCD in the accompanying figure, where the point B corresponds to the formation, at −55°, of a cryohydrate containing about $Fe_2Cl_6 + 36H_2O$, the point C to the melting-point (+37°) of the hydrate $Fe_2Cl_6,12H_2O$, and the curve CD to the fall in the temperature of crystallisation with an increase in the amount of salt or a decrease in the amount of water (in the figure the temperatures are taken along the axis of abscissæ, and the magnitude of n in the formula $nFe_2Cl_6 + 100H_2O$ along the axis of ordinates). When anhydrous Fe_2Cl_6 is added to the above hydrate ($12H_2O$), or some of the water is evaporated from the latter, very hygroscopic crystals of $Fe_2Cl_6,5H_2O$ (Fritsche) are formed; they melt at 56°, and their solubility is expressed by the curve HJ, which also presents a small branch at the end J. This again gives the fall in the temperature of crystallisation with an increase taking care as far as possible to prevent any rise of temperature.[24] The normal salt separates from the brown solution when it is concentrated

---

in the amount of Fe_2Cl_6. Besides these curves and the solubility of the anhydrous salt expressed by the line KL (up to 100°, beyond which chlorine is liberated), Roozeboom also gives the two curves, EFG and JK, corresponding to the crystallohydrates, $Fe_2Cl_6,7H_2O$ (melts at +32·5°, that is, lower than any of the others) and $Fe_2Cl_6,4H_2O$ (melts at 73·5°), which he discovered by a systematic research on the solutions of ferric chloride.

The researches of the same Dutch chemist upon the conditions of the formation of crystals from the double salt $(NH_4Cl)_4,Fe_2Cl_6,2H_2O$ are even more complete. This salt was obtained in 1839 by Fritsche, and is easily formed from a strong solution of Fe_2Cl_6 by adding sal-ammoniac, when it separates in crimson rhombic crystals, which, after dissolving in water, only deposit again on evaporation, together with the sal-ammoniac.

Roozeboom (1892) found that when the solution contains b molecules of Fe_2Cl_6 and a molecules of NH_4Cl, per 100 molecules of H_2O, then at 15° one of the following separations takes place: (1) crystals, $Fe_2Cl_6,12H_2O$, when a varies between 0 and 1·1 and b between 4·65 and 4·8, or (2) a mixture of these crystals and the double salt, when a is 1·36, and b, 4·47, or (3) the double salt, $Fe_2Cl_6,4NH_4Cl,2H_2O$, when a varies between 2 and 11·8, and b between 3·1 and 4·65, or (4) a mixture of sal-ammoniac with the iron salt (it crystallises in separate cubes, Retgers, Lehmann), when a varies between 7·7 and 10·9, and b is less than 3·38, or (5) sal-ammoniac, when a is 11·88. And as in the double salt, $a : b :: 4 : 1$, it is evident that the double salt only separates out when the ratio $a : b$ is less than 4 : 1 (i.e., when Fe_2Cl_6 predominates). The above is seen more clearly in the accompanying figure, where a, or the number of molecules of NH_4Cl per $100H_2O$, is taken along the axis of abscissæ, and b, or the number of molecules of Fe_2Cl_6, along the ordinates. The curves ABCD correspond to saturation, and present the isotherm of 15°. The portion AB corresponds to the separation of Fe_2Cl_6 (the ascending nature of this curve shows that the solubility of Fe_2Cl_6 is increased by the presence of NH_4Cl, while that of NH_4Cl decreases in the presence of Fe_2Cl_6), the portion BC to the double salt, and the portion CD to a mixture of sal-ammoniac and ferric chloride, while the straight line OF corresponds to the ratio $Fe_2Cl_6,4NH_4Cl$, or $a : b :: 4 : 1$. The portion CE shows that more double salt may be introduced into the solution without decomposition, but then the solution deposits a mixture of sal-ammoniac and ferric chloride (see Chap. XXIV., note 9a). If there were more such well-investigated cases of solutions, our knowledge of double salts, solutions, the influence of water, equilibria, isomorphous mixtures, and suchlike provinces of chemical relations might be considerably advanced. The subject belongs to the province of physical chemistry.

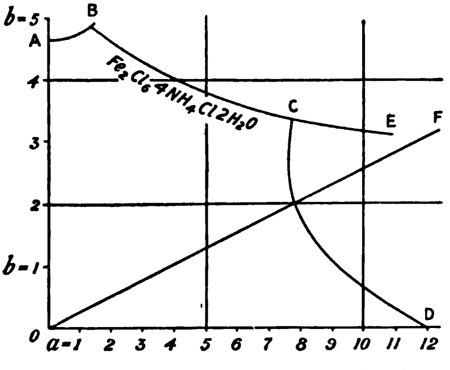


FIG. 107.—Diagram of the formation, at 15°, of the double salt $Fe_2Cl_6,4NH_4Cl,2H_2O$ or $Fe(NH_4)_2Cl_5,H_2O$. (After Roozeboom.)

[24] The normal ferric salts are decomposed by heat and even by water, forming basic salts, which may be prepared in various ways. Normal ferric hydroxide is dissolved in solutions of ferric nitrate; if these contain a double quantity of iron the basic salt is formed which contains Fe_2O_3 (in the form of hydroxide) $+2Fe_2(NO_3)_6=3Fe_2O(NO_3)_4$,

under a bell-jar over sulphuric acid. This salt, $Fe_2(NO_3)_6,9H_2O$, then crystallises in well-formed and perfectly colourless crystals,[25] which deliquesce in the air, melt at 35°, and are soluble in and decomposed by water. The decomposition may be seen from the fact that the solution is brown and does not yield the whole of the salt again, but gives

a salt of the type Fe_2OX_4. Probably water enters into its composition. With considerable quantities of ferric oxide, insoluble basic salts are obtained containing various amounts of ferric hydroxide. Thus, when a solution of the above-mentioned basic acid is boiled, a precipitate is formed containing $4(Fe_2O_3),2(N_2O_5),3H_2O$, which probably contains $2Fe_2O_2(NO_3)_2 + 2Fe_2O_3,3H_2O$. If a solution of basic nitrate is sealed in a tube and then immersed in boiling water, the colour of the solution changes just in the same way as if a solution of ferric acetate had been employed (note 22) and in the same manner as the salts of Cr_2O_3. The solution obtained smells strongly of nitric acid, and on adding a drop of sulphuric or hydrochloric acid the insoluble variety of hydrated ferric oxide is precipitated.

Normal **ferric orthophosphate** is soluble in sulphuric, hydrochloric, and nitric acids, but insoluble in others, such as, for instance, acetic acid. The composition of this salt in the anhydrous state is $FePO_4$, because in orthophosphoric acid there are three atoms of hydrogen, and iron, in the ferric state, replaces these three atoms. This salt is obtained from ferric acetate, which, with disodium phosphate, forms a *white precipitate* of $FePO_4$, containing water. If a solution of ferric chloride (yellowish-red colour) be mixed with a solution of sodium acetate in excess, the liquid assumes an intense brown colour, which demonstrates the formation of a certain quantity of ferric acetate; the disodium phosphate also forms a white gelatinous precipitate of ferric phosphate. By this means the whole of the iron may be precipitated, and the liquid, which was brown, then becomes colourless. If this normal salt be dissolved in orthophosphoric acid, the crystalline acid salt, $FeH_3(PO_4)_2$, is formed. If there be an excess of ferric oxide in the solution, the precipitate will consist of the basic salt. If ferric phosphate is dissolved in hydrochloric acid and ammonia added, on heating, a salt is precipitated which, after continued washing in water and heating (to remove the water), has the composition $Fe_4P_2O_{11}$—that is, $2Fe_2O_3,P_2O_5$. In an aqueous condition this salt may be considered as ferric hydroxide, $Fe_2(OH)_6$, in which $(OH)_3$ is replaced by the equivalent group PO_4. Whenever ammonia is added to a solution containing an excess of a ferric salt and a certain amount of phosphoric acid, a precipitate is formed containing the whole of the phosphoric acid in the mass of the ferric oxide.

Ferric oxide is characterised as a feeble base, and also by the fact of its forming double salts—for instance, **potassium iron alum**, which has a composition $Fe_2(SO_4)_3,K_2SO_4,24H_2O$, or $FeK(SO_4)_2,12H_2O$. It is obtained in the form of almost colourless or light rose-coloured large octahedra of the regular system by simply mixing solutions of potassium sulphate and the ferric sulphate obtained by dissolving ferric oxide in sulphuric acid. The rubidium iron alums readily crystallise at +2°, +3°, but melt and decompose at 38° (Erdmann). This may be taken advantage of for separating Rb from K.

[25] It would seem that all normal hydrated ferric salts are colourless, and that the brown colour peculiar to their solutions is really due to basic ferric salts. A remarkable example of the apparent change of colour of salts is represented by the ferrous and ferric oxalates. The former in a dry state has a yellow colour, although, as a rule, the ferrous salts are green, and the latter is colourless or pale green. When the normal ferric salt is dissolved in water it is, like many salts, probably decomposed by the water into acid and basic salts, and the latter communicates a brown colour to the solution. Iron alum is almost colourless, is easily decomposed by water, and is the best proof of the above assertion. A parallel study of the phenomena peculiar to ferric and chromic salts might, in my opinion, give a very useful addition to our knowledge of the aqueous solutions of salts in general.

partly basic salt. The normal salt (only stable in the presence of an excess of HNO_3) is completely decomposed with great facility by heating, even with water, at 130°, and this is made use of for removing iron (and also certain other oxides of the form R_2O_3) from many other bases (of the form RO) whose nitrates are far more stable. The ferric salts, FeX_3, in passing into ferrous salts, act as oxidising agents, as is seen from the fact that they liberate not only S from SH_2, but also iodine from KI, like many oxidising agents.[25a]

Iron forms one other oxide besides the ferric and ferrous oxides; this contains twice as much oxygen as the former, but is so very unstable that it can be obtained neither in the free state nor as a hydrate. Whenever such conditions of double decomposition occur as should allow of its separation in the free state, it decomposes into oxygen and ferric oxide. It is known in the form of salts, and is only stable in the presence of alkalies, with which it gives salts having a decidedly alkaline reaction; it is therefore a feebly acid oxide. When small pieces of iron are heated with nitre or potassium chlorate, a potassium salt of the composition K_2FeO_4 is formed. The same salt is formed when cast iron (but not pure iron) is used as an anode in a solution of potash. The hydrate corresponding with this salt should have the composition H_2FeO_4. It is called **ferric acid.** Its anhydride ought to contain FeO_3 or Fe_2O_6—twice as much oxygen as ferric oxide. If a solution of potassium ferrate be mixed with acid, the free hydrate ought to be formed, but it immediately decomposes ($2K_2FeO_4 + 5H_2SO_4 = 2K_2SO_4 + Fe_2(SO_4)_3 + 5H_2O + O_3$), oxygen being

---

[25a] The reaction $FeX_3 + KI = FeX_2 + KX + I$ proceeds comparatively slowly in solutions, is not complete (depends upon the mass), and is reversible. In this connection we may cite the following data from Seubert and Rohrer's (1894) comprehensive researches. The investigations were conducted with solutions containing $\frac{1}{10}$ gram-equivalent weights of $Fe_2(SO_4)_3$ (i.e., containing 20 grams of salt per litre), and a corresponding solution of KI, the amount of iodine liberated being determined (after the addition of starch) by a solution (also $\frac{1}{10}$ normal) of $Na_2S_2O_3$ (see Chap. XX., note 42). The progress of the reaction was expressed by the amount of iodine liberated in percentages of the theoretical amount. For instance, the following amount of iodide of potassium was decomposed when $Fe_2(SO_4)_3 + 2nKI$ was taken:

$n =$	1	2	3	6	10	20
After 15′	11·4	26·3	40·6	73·5	91·6	96·0
„ 30′	14·0	35·8	47·8	78·5	94·3	97·4
„ 1 hour	19·0	42·7	56·0	84·0	95·7	97·6
„ 10 hours	32·6	56·0	75·7	93·2	96·5	97·6
„ 48 „	39·4	67·7	82·6	93·4	96·6	97·6

Similar results were obtained for $FeCl_3$, but there the amount of iodine liberated was somewhat greater. Similar results were also obtained by increasing the mass of FeX_3 relatively to that of the KI, and by replacing it by HI (see Chap. XXI., note 26). Such instances as these show that the rate of chemical reaction and the influence of the reacting masses are questions of special interest to modern theoretical chemistry.

evolved. If a small quantity of acid is taken, or if a solution of potassium ferrate is heated with solutions of other metallic salts, ferric oxide is separated—for instance :

$$2CuSO_4 + 2K_2FeO_4 = 2K_2SO_4 + O_3 + Fe_2O_3 + 2CuO.$$

Both these oxides are of course deposited in the form of hydrates. This shows that not only the hydrate H_2FeO_4, but also the salts of the heavy metals corresponding with this higher oxide of iron, are not formed by reactions of double decomposition. But the barium salt, which is only slightly soluble in water, is formed by adding $BaCl_2$, which points to a certain resemblance to sulphuric acid. The solution of potassium ferrate naturally acts as a powerful oxidising agent; for instance, it transforms manganous oxide into the dioxide, sulphurous into sulphuric acid, oxalic acid into carbonic anhydride and water, &c.[26]

Iron thus combines with oxygen in three proportions: RO, R_2O_3, and RO_3. It might have been expected that there would be intermediate stages, RO_2 (corresponding to pyrites, FeS_2) and R_2O_5, but for iron these are unknown.[26a] The lower oxide has a distinctly basic character, the higher is feebly acid. The only one which is stable in the free state is ferric oxide, Fe_2O_3; the suboxide, FeO, absorbs oxygen, and ferric anhydride, FeO_3, evolves it. It is also the same with other elements ; the character of each is determined by the relative

---

[26] If chlorine is passed through a strong solution of potassium hydroxide in which hydrated ferric oxide is suspended, the turbid liquid acquires a dark pomegranate-red colour and contains potassium ferrate: $10KHO + Fe_2O_3 + 3Cl_2 = 2K_2FeO_4 + 6KCl + 5H_2O$. The chlorine must not be in excess, otherwise the salt is again decomposed, although the mode of decomposition is unknown; probably ferric chloride and potassium chlorate are formed.

[26a] After Mond and his assistants obtained the remarkable volatile compound $Ni(CO)_4$ (described later), it was shown by Mond and Quincke (1891), and also by Berthelot, that iron, under certain conditions, in a stream of carbonic oxide, also volatilises and forms a compound like that given by nickel. Roscoe and Scudder then showed that when water gas is passed through and kept under pressure (8 atmospheres) in iron vessels a portion of the iron volatilises from the sides of the vessel, and that when the gas is burnt it deposits a certain amount of oxides of iron (the same result is obtained with ordinary coal gas, which contains a small amount of CO). To obtain the volatile **compound of iron with carbonic oxide**, Mond prepared a finely divided iron by heating the oxalate in a stream of hydrogen, and after cooling this to 80° – 45°, passed CO over it. The iron then formed (although very slowly) a volatile compound of the composition $Fe(CO)_5$ (as though it answered to a very high type, FeX_{10}), which when cooled condenses into a liquid (slightly coloured, probably owing to incipient decomposition), of sp. gr. 1·47, which solidifies at –21°, boils at about 103°, and has a vapour density (about 6·5 with respect to air) corresponding with the above formula; it decomposes at 180°. Water and dilute acids do not act upon it, but it decomposes under the action of light and forms a hard, non-volatile crystalline yellow compound, $Fe_2(CO)_7$, which decomposes at 80° and again forms $Fe(CO)_5$.

degree of stability of the known oxides. The salts FeX_2 correspond with the suboxide, the salts FeX_3 or Fe_2X_6 with the sesquioxide, and FeX_6 represents those of ferric acid, as its potassium salt is $FeO_2(OK)_2$, corresponding with K_2SO_4, K_2MnO_4, K_2CrO_4, &c. Iron therefore forms compounds of the types FeX_2, FeX_3, and FeX_6, but this latter, like the type NX_5, does not appear separately, but only when X represents heterogeneous elements or groups; for instance, for nitrogen in the form of $NO_2(OH)$, NH_4Cl, &c., for iron in the form of $FeO_2(OK)_2$. But still the type FeX_6 exists, and therefore FeX_2 and FeX_3 are compounds which, like ammonia, NH_3, are capable of further combinations up to FeX_6; this is perhaps also partly seen in the property of ferrous and ferric salts of forming compounds with water of crystallisation, besides double and basic salts, the stability of which is determined by the quality of the elements included in the types FeX_2 and FeX_3. It is therefore to be expected that there should be complex compounds derived from ferrous and ferric oxides. Amongst these the series of cyanogen compounds is particularly interesting; their formation and character are determined not only by the property which iron possesses of forming complex types, but also by the similar faculty of the cyanogen compounds, which, like nitriles (Chap. IX.), have clearly developed properties of polymerisation and in general of forming complex compounds.[27]

In the cyanogen compounds of iron, two degrees might be expected: $Fe(CN)_2$, corresponding with ferrous oxide, and $Fe(CN)_3$, corresponding with ferric oxide. There are actually, however, many other known compounds, intermediate and far more complex. They correspond with the double salts so easily formed by metallic cyanides. The two following double salts are particularly well known, very stable, often used, and easily prepared. **Potassium ferrocyanide** or **yellow prussiate of potash,** a double salt of cyanide of potassium and ferrous cyanide, has the composition $FeC_2N_2,4KCN$; its crystals contain 3 mols. of water: $K_4FeC_6N_6,3H_2O$. The other is **potassium ferricyanide** or **red prussiate of potash.** It is also known as **Gmelin's salt,** and contains cyanide of potassium with ferric cyanide; its composition is $Fe(CN)_3,3KCN$ or $K_3FeC_6N_6$. Its crystals do not contain water. It is obtained from

---

[27] Some light may be thrown upon the faculty of Fe of forming various compounds with CN, by the fact that Fe not only combines with carbon but also with nitrogen. *Nitride of iron*, Fe_2N, was obtained by Fowler by heating finely powdered iron in a stream of NH_3 at the temperature of melting lead, but this experiment has not been verified. Judging from their reactions, the ferricyanides belong to the class of 'complex' compounds which present some analogy to the organic compounds, for the Fe and CN in the ferricyanides do not react in the usual manner, like the acid elements in organic compounds.

the first by the action of chlorine, which removes one atom of the potassium. A whole series of other **ferrocyanic compounds** correspond with these ordinary salts. Before treating of the preparation and properties of these two remarkable and very stable salts, it must be observed that with ordinary reagents neither of them gives the same double decompositions as the other ferrous and ferric salts, and they both present a series of remarkable and original reactions.[27a] Thus solutions of these salts have a neutral reaction (that of KCN is alkaline) and are unchanged by air, dilute acids, or water (unlike potassium cyanide). Caustic alkalies do not give a precipitate of ferrous or ferric hydroxide from solutions of these salts, which are also not precipitated by sodium carbonate. This led the earlier investigators to recognise special independent groupings in them. The yellow prussiate was considered to contain the complex radicle FeC_6N_6 combined with potassium, namely, with K_4, while in the red prussiate the same complex is combined with K_3. This was confirmed by the fact that whilst in both salts any other metal, even hydrogen, might be substituted for potassium, the iron remained unchangeable, just as the nitrogen in cyanogen, ammonium, and nitrates does not enter into double decomposition, being in the state of the complex radicles, CN, NH_4, NO_2. Such a representation is, however, quite superfluous for the explanation of the peculiarities in the reactions of such compounds as double salts. If a magnesium salt which can be precipitated by potassium hydroxide does not form a precipitate in the presence of ammonium chloride, it is very clear that it is owing to the formation of a soluble double salt which is not decomposed by alkalies. And there is no necessity to account for the peculiarity of reaction of a double salt by the formation of a new complex radicle. In the same way also, in the presence of an excess of tartaric acid, cupric salts do not form a precipitate with potassium hydroxide, because a double salt is formed. These peculiarities are more easily

---

[27a] Which is, indeed, the property of the so-called 'complex' compounds, concerning which I have already given, and shall subsequently give my opinion. I think the recognition of complex radicles or residues is mostly and generally a simple statement or expression of a fact, and helps very little towards gaining a deeper insight into the properties of chemical compounds, &c., which ought to be the chief aim of all perfect knowledge. For example, the recognition of $Fe(CN)_6$ does not show that this residue combines with K_3 and K_4; it does not exist in a free state, does not form $R(OH)_n$ or $R(NH_2)_n$, &c., and those qualities proper to its compounds are most simply and advantageously understood by simply recognising the existence of double salts of ferrous and ferric oxides, and by recognising that, in general, complex molecules composed of polyatomic atoms readily build themselves up in various ways (isomerise) as is seen both in the 'complex' and in carbon compounds. A comprehension of the structure and mode of building up will require as complete a study of the reactions as exists for the organic compounds. These considerations incline me to the opinion that the recognition of a radicle, $Fe(CN)_6$, is unnecessary.

understood in the case of cyanogen compounds than in all others, because all cyanogen compounds, as unsaturated compounds, show a marked tendency to complexity. This tendency is satisfied in double salts. The appearance of a peculiar character in double cyanides is the more easily understood, since in the case of potassium cyanide itself, and also in hydrocyanic acid, a great many peculiarities have been observed which are not encountered in those haloid compounds, potassium chloride and hydrochloric acid, with which it was *usual* to compare cyanogen compounds. These peculiarities become more comprehensible on comparing cyanogen compounds with ammonia compounds. Thus in the presence of ammonia the reactions of many compounds change considerably. If in addition to this it is remembered that the presence of many carbon (organic) compounds frequently completely disturbs the reactions of salts, the peculiarities of certain double cyanides will appear still less strange, because they contain carbon. The fact that the presence of carbon or another element in the compound produces a change in the reactions may be compared with the action of oxygen, which, when entering into a combination, also very materially changes the nature of reactions. Chlorine is not detected by silver nitrate when it is in the form of potassium chlorate, $KClO_3$, as it is detected in potassium chloride, KCl. The iron in ferrous and ferric compounds varies in its reactions. In addition to the above-mentioned facts, consideration ought to be given to the circumstance that the easy mutability of nitric acid undergoes modification in its alkali salts, and in general the properties of a salt often differ much from those of the acid. Every double salt ought to be regarded as a peculiar kind of saline compound : potassium cyanide is, as it were, a basic, and ferrous cyanide an acid, element. They may be more or less unstable in the separate state, but form a stable double compound when combined together ; the act of combination disengages the energy of the elements, and they, so to speak, saturate each other. Of course, all this is not a definite explanation, but then the supposition of a special complex radicle can even less be regarded as such.

Potassium ferrocyanide, $K_4FeC_6N_6$, is very easily formed by mixing solutions of ferrous sulphate and potassium cyanide. First, a white precipitate of ferrous cyanide, FeC_2N_2, is formed, which becomes blue on exposure to air, but is soluble in an excess of potassium cyanide, forming the ferrocyanide. The same yellow prussiate is obtained on heating nitrogenous animal charcoal or animal matters—such as horn, leather cuttings, &c.—with potassium carbonate in iron vessels,[27b]

[27b] The sulphur of the animal refuse here forms the compound $FeKS_2$, which, by the action of potassium cyanide, yields potassium sulphide, thiocyanate, and ferrocyanide.

the mass formed being afterwards boiled with water with exposure to air, potassium cyanide first appearing, which gives yellow prussiate. The animal charcoal may be exchanged for wood charcoal, permeated with potassium carbonate and heated in nitrogen or ammonia; the mass thus produced is then boiled in water with ferric oxide.[28] In this manner it is manufactured on the large scale, and is called **yellow prussiate** (*prussiate de potasse, Blutlaugensalz*).

It is easy to substitute other metals for the potassium in the yellow prussiate by double decomposition. The hydrogen salt or **hydroferrocyanic acid**, $H_4FeC_6N_6$, is obtained by mixing strong solutions of yellow prussiate and hydrochloric acid. If ether is added and the air excluded, the acid is obtained directly in the form of a white scarcely crystalline precipitate which becomes blue on exposure to air (as ferrous cyanide does from the formation of blue compounds of ferrous and ferric cyanides, on which account it is used in cotton printing). It is soluble in water and alcohol, but not in ether, has marked acid properties, and decomposes carbonates, thus rendering it easily possible to prepare ferrocyanides of the metals of the alkalies and alkaline earths; these are readily soluble, have a neutral reaction, and resemble the yellow prussiate. Solutions of these salts form precipitates with the salts of other metals, because the ferrocyanides of the heavy metals are insoluble. Either the whole of the potassium, K_4, of the yellow prussiate, or only a part of it, is exchanged for an equivalent quantity of the heavy metal. Thus, when a cupric salt is added to a solution of yellow prussiate, a red precipitate is obtained which still contains half the potassium of the yellow prussiate:

$$K_4FeC_6N_6 + CuSO_4 = K_2CuFeC_6N_6 + K_2SO_4.$$

But if the process be reversed (the salt of copper being then in excess), the whole of the potassium will be exchanged for copper, forming a reddish-brown precipitate, $Cu_2FeC_6N_6,9H_2O$. This reaction and those similar to it[28a] are very sensitive, and may be used for detecting

---

[28] Potassium ferrocyanide may also be obtained from Prussian blue by boiling with a solution of potassium hydroxide, and from the ferricyanide by the action of alkalies and reducing substances (because the red prussiate is a ferric salt, and is reduced to a ferrous salt), &c. In many works (especially in Germany and France) yellow prussiate is prepared from the mass, containing oxide of iron, employed for purifying coal gas (Vol. I.), which generally contains cyanogen compounds. About 2 per cent. of the nitrogen contained in coal is converted into cyanogen, which forms Prussian blue and thiocyanates in the mass used for purifying the gas. On evaporation, the solution yields large yellow crystals containing 3 molecules of water, which is easily expelled by heating above 100°. A hundred parts of water at the ordinary temperature are capable of dissolving 25 parts of this salt; its sp. gr. is 1·83. When ignited it forms potassium cyanide and iron carbide, FeC_2 (Chap. XIII., note 12). Oxidising substances change it into potassium ferricyanide. With strong sulphuric acid it gives carbonic oxide, and with dilute sulphuric acid, when heated, prussic acid is evolved.

[28a] In the interaction of $ZnSO_4$ and yellow prussiate, Miller and Danziger (1902)

metals in solution, more especially as the colour of the precipitate very often shows a marked variation when one metal is exchanged for another. Zinc, cadmium, lead, antimony, tin, silver, cuprous and aurous salts form **white precipitates**; cupric, uranium, titanium, and molybdenum salts, **reddish-brown**; those of nickel, cobalt, and chromium, **green** precipitates; **with ferrous salts**, ferrocyanide forms, as has been already mentioned, a **white** precipitate—namely, $Fe_2FeC_6N_6$, or FeC_2N_2—which turns blue on exposure to air, and with ferric salts a **blue precipitate** called **Prussian blue.** Here the potassium is replaced by iron, the reaction being expressed thus: $2Fe_2Cl_6+3K_4FeC_6N_6=12KCl+Fe_4Fe_3C_{18}N_{18}$, the latter formula expressing the composition of Prussian blue. It is therefore the compound $4Fe(CN)_3+3Fe(CN)_2$. The yellow prussiate is prepared in chemical works on a large scale, especially for the manufacture of this blue pigment, which is used for dyeing cloth and other fabrics and also as one of the ordinary blue paints. It is insoluble in water, and the stuffs are therefore dyed by soaking them first in a solution of a ferric salt and then in a solution of yellow prussiate. If, however, an excess of yellow prussiate be present, complete substitution between potassium and iron does not occur, and **soluble Prussian blue** is formed, $KFe_2(CN)_6 = KCN,Fe(CN)_2,Fe(CN)_3$. This blue salt is colloidal and soluble in pure water, and is precipitated when other salts—for instance, potassium or sodium chloride—are present even in small quantities, and is therefore first obtained as a precipitate.[29]

Potassium ferricyanide, or **red prussiate** of potash, $K_3FeC_6N_6$, is

---

obtained precipitates containing different amounts of Fe, K, and Zn, according as one or the other original salt was in excess, or according to whether acids, ammonia, &c., were present. With excess of the zinc salt and after washing with a solution of ammonia, $Zn_2Fe(CN)_6$ was obtained, and with an excess of the yellow prussiate a salt which in the limit had the composition $K_2Zn_3Fe_2(CN)_{12}$.

[29] Skraup obtained this salt both from potassium ferrocyanide with ferric chloride and from ferricyanide with ferrous chloride, which evidently shows that it contains iron in both the ferric and ferrous states. With ferrous chloride it forms Prussian blue, and with ferric chloride Turnbull's blue.

Prussian blue was discovered in the beginning of the eighteenth century by Diesbach. Prussian blue has not a crystalline structure; it forms a blue mass with a copper-red metallic lustre. Both acids and alkalies act on it. The action is at first confined to the ferric salt it contains. Thus, alkalies form ferric oxide and ferrocyanide in solution: $2Fe_2C_6N_6,3FeC_2N_2+12KHO=2(Fe_2O_3,3H_2O)+3K_4FeC_6N_6$. Prussian blue is soluble in an aqueous solution of oxalic acid, forming blue ink. In air, when exposed to the action of light, it fades; but in the dark it again absorbs oxygen and becomes blue, which fact is also sometimes noticed in blue cloth. An excess of potassium ferrocyanide renders Prussian blue soluble in water, although insoluble in various saline solutions—that is, it converts it into the soluble variety. Strong hydrochloric acid also dissolves Prussian blue.

called 'Gmelin's salt,' because this savant obtained it by the action of chlorine on a solution of the yellow prussiate: $K_4FeC_6N_6+Cl=K_3FeC_6N_6+KCl$. The reaction is due to the ferrous salt being changed by the action of the chlorine into a ferric salt. It separates from solutions in anhydrous well-formed prisms of a red colour, but the solution has an olive colour; 100 parts of water, at 10°, dissolve 37 parts of the salt, and at 100°, 78 parts.[30] The red prussiate gives a blue precipitate with ferrous salts, called **Turnbull's blue,** very much like Prussian blue (and the soluble variety), because it also contains ferrous cyanide and ferric cyanide, although in another proportion, being formed according to the equation: $3FeCl_2+2K_3FeC_6N_6=6KCl+Fe_3Fe_2C_{12}N_{12}$, or $3FeC_2N_2,Fe_2C_6N_6$: in Prussian blue we have Fe_7Cy_{18}, and here Fe_5Cy_{12}. A ferric salt ought to form ferric cyanide $Fe_2C_6N_6$, with red prussiate; but ferric cyanide is soluble, and therefore no precipitate is obtained, and the liquid only becomes brown.[31]

---

[30] An excess of chlorine must not be employed in preparing this compound, otherwise the reaction goes further. It is easy to find out when the action of the chlorine on potassium ferrocyanide must cease; it is only necessary to take a sample of the liquid and add a solution of a ferric salt to it. If a precipitate of Prussian blue is formed, more chlorine must be added, as there is still some undecomposed ferrocyanide, for the ferricyanide does not give a precipitate with ferric salts. Potassium ferricyanide, like the ferrocyanide, readily exchanges its potassium for hydrogen and various metals by double decomposition. With the salts of tin, silver, and mercury it forms yellow precipitates, and with those of uranium, nickel, cobalt, copper, and bismuth brown precipitates. The lead salt, under the action of sulphuretted hydrogen, forms lead sulphide and a hydrogen salt or acid, $H_3FeC_6N_6$, corresponding with potassium ferricyanide, which is soluble, crystallises in red needles, and resembles hydroferrocyanic acid, $H_4FeC_6N_6$. Under the action of reducing agents—for instance, sulphuretted hydrogen or copper—potassium ferricyanide is changed into ferrocyanide, especially in the presence of alkalies, and forms a rather energetic **oxidising agent**—capable, for instance, of changing manganous oxide into dioxide, of bleaching tissues, &c.

[31] It is important to mention a series of readily crystallisable salts formed by the action of nitric acid on potassium and other ferrocyanides and ferricyanides. These salts contain the elements of nitric oxide, and are therefore called **nitro- (nitroso-) ferricyanides** (nitro-prussides). Generally a crystalline sodium salt is obtained, $Na_2FeC_5N_6O,2H_2O$. In its composition this salt differs from the red sodium salt, $Na_3FeC_6N_6$, by the fact that in it one molecule of sodium cyanide, NaCN, is replaced by nitric oxide, NO. In order to prepare it, powdered potassium ferrocyanide is mixed with five-sevenths of its weight of nitric acid diluted with an equal volume of water. The mixture is at first left at the ordinary temperature, and then heated on a water-bath. Here ferricyanide is first of all formed (as shown by the liquid giving a precipitate with ferrous chloride), this disappearing later (no precipitate with ferrous chloride), and forming a green precipitate. The liquid, when cooled, deposits crystals of nitre, from which it is then strained off and mixed with sodium carbonate, boiled, filtered, and evaporated; sodium nitrate and the salt described are deposited in crystals. It separates in prisms of a red colour. Alkalies and salts of the alkaline earths do not give precipitates, but soluble compounds, but the salts of iron, zinc, copper, and silver form precipitates in which the sodium is replaced by these metals. It is remarkable that the sulphides of the alkali metals give with this salt an intense bright purple coloration. This

If chlorine and sodium are representatives of independent groups of elements, the same may also be said of iron. Its nearest analogues show, besides a similarity in character, a likeness as regards physical properties and a proximity in atomic weight. Iron occupies a medium position amongst its nearest analogues, with respect both to properties and to the faculty of forming saline oxides, and also as regards atomic weight. On the one hand, cobalt, 59, and nickel, 59, approach iron, 56 ; they are metals of a more basic character, they do not form stable acids or higher degrees of oxidation, and are a transition to copper, 63, and zinc, 65. On the other hand, manganese, 55, and chromium, 52, forming both basic and acid oxides, are the nearest to iron. In addition to having atomic weights approximately alike, chromium, manganese, iron, cobalt, nickel, and copper have also nearly the same specific gravity, so that the atomic volumes and the molecules of their analogous compounds are also near to one another (see table at the beginning of this volume). Besides this, the likeness between the above-mentioned elements is also seen from the following:

They form suboxides, RO, which are fairly energetic bases, isomorphous with magnesia—for instance, the salt $RSO_4,7H_2O$, akin to $MgSO_4,7H_2O$ and $FeSO_4,7H_2O$, or to sulphates containing less water; with alkali sulphates all form double salts crystallising with $6H_2O$; all are capable of forming ammonium salts, &c. The lower oxides, in the cases of nickel and cobalt, are tolerably stable, and are not easily oxidised (the nickel compound with more difficulty than cobalt, a transition to copper) ; with manganese, and especially with chromium, they are more easily oxidised than with iron and pass into higher oxides. They all also form oxides of the form R_2O_3, and with nickel and cobalt, these oxides are very unstable, and are more easily reduced than ferric oxide; but, in the case of chromium, it is very stable, and forms the ordinary kind of salts. Chromium, manganese, and iron are oxidised by alkali and oxidising agents, forming salts like Na_2SO_4 ; but cobalt and nickel are difficult to oxidise, and their acids are not known

---

series of compounds was discovered by Gmelin and studied by Playfair and others (1849).

This series to a certain extent resembles the nitro-sulphide series described by Roussin. Here the primary compound consists of black crystals, which are obtained as follows:—Solutions of potassium hydrosulphide and nitrate are mixed, and the mixture is agitated while ferric chloride is added, then boiled and filtered; on cooling, **black crystals** are deposited, having the composition $Fe_6S_5(NO)_{10},H_2O$ (Rosenberg), or, according to Demel, $FeNO_2,NH_2S$. They have a slightly metallic lustre, and are soluble in water, alcohol, and ether. They absorb the latter as easily as calcium chloride absorbs water. In the presence of alkalies these crystals remain unchanged, but with acids they evolve nitric oxides. There is no necessity to describe these series in detail, because their connection with other compounds is not yet clear, and they have not yet any application.

with any certainty, and are, in all probability, still less stable than the ferrates. Cr, Mn, and Fe form compounds R_2Cl_6 which are like Fe_2Cl_6 in many respects ; in Co this faculty is weaker and in Ni it has almost disappeared. The cyanogen compounds, especially of manganese and cobalt, are very near akin to the corresponding ferrocyanides. The oxides of nickel and cobalt are more easily reduced to metal than those of iron, but those of manganese and chromium are not reduced so readily as those of iron, and the metals themselves are not easily obtained in a pure state ; they are capable of forming varieties resembling cast iron. The metals Cr,Mn,Fe,Co, and Ni have an iron-grey colour and are very difficult to melt, but nickel and cobalt can be melted in the reverberatory furnace and are more fusible than iron, whilst chromium is more difficult to melt than platinum (Deville). These metals decompose water, but with greater difficulty as the atomic weight rises, forming a transition to copper, which does not decompose water. The **compounds** of all these metals **have various colours**, which are sometimes very bright, especially in the higher stages of oxidation.

These metals of the iron group are often met with together in nature. Manganese nearly everywhere accompanies iron, and iron is always an ingredient in the ores of manganese. Chromium is found principally as chrome ironstone—that is, a peculiar kind of magnetic oxide in which Fe_2O_3 is replaced by Cr_2O_3.

Nickel and cobalt are as inseparable companions as iron and manganese, and Ni is found with iron in meteorites. The similiarity between them even extends to such remote properties as magnetic qualities. In this series of metals we find those which are the most magnetic : iron, cobalt, and nickel. There is even a magnetic oxide among the chromium compounds, such being unknown in the other series. Nickel easily becomes passive in strong nitric acid. It absorbs hydrogen in just the same way as iron does. In short, in the series Cr, Mn, Fe, Co, and Ni, there are many points in common, although there are many differences, as will be seen still more clearly on becoming acquainted with cobalt and nickel.

In nature **cobalt** is principally found in combination with arsenic and sulphur. *Cobalt arsenide*, or *cobalt speiss*, $CoAs_2$, is found in brilliant crystals of the regular system, principally in Saxony. *Cobalt glance*, $CoAs_2CoS_2$, resembles it very much, and also belongs to the regular system ; it is found in Sweden, Norway, and the Caucasus. *Kupfernickel* is an ore containing nickel and arsenic, but of a different composition from cobalt arsenide, having the formula NiAs ; it is found in Bohemia and Saxony. It has a copper-red colour and is rarely crystalline ; it is so called because the miners of Saxony first mistook it for an ore of copper (*Kupfer*), but were unable to extract copper from it. *Nickel glance*, $NiS_2,NiAs_2$, corresponding with cobalt glance, is also known. Nickel accompanies the ores of cobalt, and cobalt those of nickel, so that both metals are found together. The ores of cobalt are worked in the Caucasus in the government of Elizavetopolsk. Nickel ores containing aqueous hydrated nickel silicate are found in the Ural (Revdansk). Large quantities of a similar ore are exported into Europe from New Caledonia. Both ores contain about 12 per cent. of Ni. *Garnierite*, $(RO)_5(SiO_2)_4,1\frac{1}{2}H_2O$, where R=Ni and Mg, predominates in the New Caledonian ore. Large deposits of nickel have been discovered in Canada, where the ore (as nickeliferous pyrites) is free from arsenic. Cobalt is principally worked up into cobalt compounds, but nickel is generally reduced to the metallic state, in which it is now often used for alloys—for instance, with iron (nickel steel) for coinage in many European States, and for plating other metals, because it does not oxidise in the air. Cobalt arsenide and cobalt glance are principally used for the preparation of cobalt compounds; they are first sorted by discarding the rocky matter, and then roasted. During this process most of the sulphur and arsenic disappears; the arsenious anhydride volatilises with the sulphurous anhydride and the metal also oxidises.[32] It is a simple matter to obtain nickel and

---

[32] The residue from the roasting of cobalt ores is called *zaffre*, and is often met with in commerce. From this the purer compounds of cobalt may be prepared. The ores of nickel are also first roasted, and the oxides dissolved in acid, nickelous salts being then obtained.

The further treatment of cobalt and nickel ores is facilitated if the arsenic can be almost entirely removed, which may be effected by roasting the ore a second time with a small addition of nitre and sodium carbonate; the nitre combines with the arsenic, forming an arsenious salt, which may be extracted with water. The remaining mass is dissolved in hydrochloric acid, mixed with a small quantity of nitric acid. Copper, iron, manganese, nickel, cobalt, &c., pass into solution. By passing hydrogen sulphide through the solution, copper, bismuth, lead, and arsenic are deposited as metallic sulphides; but iron, cobalt, nickel, and manganese remain in solution. If an alkaline solution of bleaching powder be then added to the remaining solution, the whole of the manganese will first be deposited in the form of dioxide, then the cobalt as hydrated cobaltic oxide, and finally the nickel also. It is, however, impossible to rely on this method for effecting a complete separation, the more so since the higher oxides of the three above-mentioned metals all have a black colour; but after a few trials it will be easy to find how much bleaching powder is required to precipitate the manganese, and the amount which will precipitate all the cobalt. The manganese may also be separated from cobalt by precipitation from a mixture of the solutions of both metals (in the form of the 'ous' salts) with ammonium sulphide and then treating the precipitate with acetic acid or dilute hydrochloric acid, in which manganese sulphide is easily soluble and cobalt sulphide almost insoluble. Further particulars relating to the separation of cobalt from nickel may be found in treatises on analytical chemistry. In practice it is usual to rely on the rough method of separation founded on the fact that nickel is more easily reduced and more difficult to oxidise than cobalt. The New Caledonian ore is smelted with $CaSO_4$ and $CaCO_3$ on coke, and a metallic regulus is obtained containing all the Ni, Fe and S cobalt from their oxides. In order to obtain the latter, solutions of their salts are treated with sodium carbonate and the precipitated carbonates are heated ; the suboxides are thus obtained, and these latter are reduced in a stream of hydrogen, or even by heating with ammonium chloride. They easily oxidise when in the state of powder. When the chlorides of nickel and cobalt are heated in a stream of hydrogen, the metal is deposited in brilliant scales. *Nickel is always much more easily and quickly reduced than cobalt,* and, when in a state of powder (reduced by hydrogen), acts in many cases as a contact substance like platinum black. Nickel melts more easily than cobalt, and this even furnishes a means of testing the heating powers of a reverberatory furnace. Cobalt fuses at a temperature only a little lower than that at which iron does. In general, cobalt is more nearly allied to iron than nickel, and the latter more nearly to copper.[32a] Both nickel and cobalt have magnetic properties like iron, but Co is less magnetic than Fe, and Ni still less so. The specific gravity of nickel reduced by hydrogen is 9·1 and that of cobalt 8·9. Fused cobalt has a specific gravity of 8·5, the density of ordinary nickel being almost the same. Nickel has a greyish silvery-white colour ; it is brilliant and very ductile, so that the finest wire may be easily drawn from it. This wire has a resistance to tension equal to that of iron wire. The beautiful colour of nickel and the high polish which it is capable of receiving and retaining, as it does not oxidise, render it a useful metal for many purposes, and in many ways it resembles silver.[32b] It is now very common to cover

---

This is roasted with SiO_2, which converts all the iron into slag, whilst the Ni remains combined with the S ; this residue on further roasting gives NiO, which is reduced by the carbon to metallic Ni.

For manufacturing purposes somewhat impure cobalt compounds are frequently used, which are converted into **smalt.** This is glass containing a certain amount of cobalt oxide ; the glass acquires a bright blue colour from this addition, so that when powdered it may be used as a blue pigment ; it is also unaltered at high temperatures, so that it used to take the place now occupied by Prussian blue, ultramarine, &c. At present smalt is almost exclusively used for colouring glass and china. To prepare smalt, zaffre is fused in a crucible with quartz and potassium carbonate. A fused mass of cobalt glass is thus formed, and a metallic mass remains at the bottom of the crucible, containing almost all the other metals, arsenic, nickel, copper, silver, &c. This metallic mass is called **speiss,** and is used as nickel ore. Smalt usually contains 70 per cent. of silica, 25 of potash and soda, and about 5 to 6 of cobaltous oxide.

[32a] All we know respecting the relations of Co and Ni to Fe and Cu confirms the fact that Co is more closely related to Fe and Ni to Cu ; and as the atomic weight of Fe is 56 and that of Cu 63, it would be expected, according to the principles of the periodic system, that the atomic weight of Co would be about 59, whilst that of Ni should be greater than that of Co but less than that of Cu—i.e., about 60. However, as yet the majority of the determinations of the atomic weights of Co and Ni give a different result, but they hardly comply with the desired degree of accuracy, as has been already mentioned in Chap. XV., note 25.

[32b] For instance, the alkalies may be fused in nickel vessels as well as in silver,

other metals with a layer of nickel (nickel plating). This is done by a process of electro-plating, using a solution of a nickel salt. The colour of cobalt is dark and redder; it is also ductile, and has a greater tensile resistance than iron. Dilute acids act very slowly on nickel and cobalt; nitric acid may be considered as the best solvent for them. The solutions in every case contain salts corresponding with the ferrous salts—that is, the **salts** CoX_2, NiX_2, corresponding with the suboxides of these metals. These salts are similar in their types to those of magnesium and iron. The salts of nickel when crystallising with water have a green colour, and form bright-green solutions, but in the anhydrous state they most frequently have a yellow colour; those of cobalt are generally rose-coloured, and mostly blue when in the anhydrous state. Their aqueous solutions are rose-coloured. Cobaltous chloride is freely soluble in alcohol, and forms a solution of an intense blue colour.[33]

If a solution of potassium hydroxide be added to a solution of a

---

because they have no action upon either metal. Nickel, like silver, is not acted upon by dilute acids. Only nitric acid dissolves both metals well. Nickel is harder, and fuses at a higher temperature than silver. For castings, a small quantity of magnesium (0·001 part by weight) is added to nickel to render it more homogeneous (just as aluminium is added to steel).

[33] The change of colour is dependent in all probability on the combination with water. It enables a solution of cobalt chloride to be used as sympathetic ink. If something be written with cobalt chloride on white paper, it will be invisible on account of the feeble colour of the solution, and when dry nothing can be distinguished. If, however, the paper be heated before the fire, the rose-coloured salt will be changed into a less hydrous blue salt, and the writing will become quite visible, but will fade away when cool.

The change of colour which takes place in solutions of $CoCl_2$ under the influence not only of solution in water or alcohol, but also of a change of temperature, is a characteristic of all the halogen salts of cobalt. Crystalline iodide of cobalt, $CoI_2,6H_2O$, gives a dark-red solution between −22 and +20°; above +20° the solution turns brown and passes from olive to green; and from +35° to 320° the solution remains green. According to Étard (1891) the change of colour is due to the fact that at first the solution contains the hydrate $CoI_2,6H_2O$, and that above 35° it contains $CoI_2,4H_2O$, which can therefore be crystallised from the solutions; the former at ordinary temperature and the latter on heating the solution. A solution of the hexahydrated chloride of cobalt, $CoCl_2,6H_2O$, is rose-coloured between −22° and +25°; but the colour changes at +25°, and passes through all the tints between red and blue up to 50°; a true blue solution is only obtained at 55°, and this colour remains up to 300°. This true blue solution contains a hydrate, $CoCl_2,2H_2O$ or $CoCl_2,H_2O$, according to Potilitzin.

This is similar to what we have repeatedly seen—that aqueous solutions (for instance, Chap. XXII., note 23, for Fe_2Cl_6) deposit different crystallo-hydrates at different temperatures, and that the amount of water in the hydrate decreases as the temperature t rises. Nor is it exceptional that the colour of a salt varies according as it contains different amounts of H_2O. But in this instance it is characteristic that the change of colour takes place in solution in the presence of an excess of water. This apparently shows that the actual solution may contain either $CoCl_2,6H_2O$ or $CoCl_2,2H_2O$. And as we know that a solution may contain both metaphosphoric, PHO_3, and orthophosphoric acid, $H_3PO_4 = HPO_3 + H_2O$, as well as certain other anhydrides, the question of the state cobalt salt, a blue precipitate of the basic salt will be formed. If a solution of a cobalt salt be heated almost to the boiling-point, and the solution be then mixed with a boiling solution of an alkali hydroxide,

of substances in solutions becomes still more complicated (see the salts of Cr_2O_3). Perhaps the rose-tint is peculiar to CoX_2,nH_2O and the blue to $Co(OH)_2HX$?

It is remarkable that a solution of cobalt nitrate acts, as has long been known, as an antidote in cases of poisoning by prussic acid or potassium cyanide.

Nickel sulphate crystallises from neutral solutions at a temperature of from 15° to 20° in *rhombic* crystals containing $7H_2O$. Its form approaches very closely to that of the salts of zinc and magnesium. The planes of a vertical prism for magnesium salts are inclined at an angle of 90° 30′, for zinc salts at an angle of 91° 7′, and for nickel salts at an angle of 91° 10′. Such is also the form of the zinc and magnesium selenates and chromates. Cobalt sulphate containing 7 molecules of water is deposited in crystals of the *monoclinic* system, like the corresponding salts of iron and manganese. The angle of a vertical prism for the iron salt is 82° 20′, for cobalt, 82° 22′, and the inclination of the horizontal pinacoid to the vertical prism for the iron salt is 99° 2′, and that for the cobalt salt, 99° 36′. All the isomorphous mixtures of the salts of magnesium, iron, cobalt, nickel and manganese have the same form if they contain 7 mols. of H_2O and iron or cobalt predominate, whilst if there is a preponderance of magnesium, zinc, or nickel, the crystals have a rhombic form like magnesium sulphate. Hence these sulphates are **dimorphous**, but for some the one form is more stable and for others the other. Brooke, Moss, Mitscherlich, Rammelsberg, and Marignac have explained these relations. Brooke and Mitscherlich also supposed that $NiSO_4,7H_2O$ is capable of assuming not only these forms, but also that of the *tetragonal* system, because it is deposited in this form from acid, and especially from slightly heated, solutions (30° to 40°). But Marignac demonstrated that the tetragonal crystals do not contain 7, but 6, molecules of water, $NiSO_4,6H_2O$. He also observed that a solution evaporated at 50° to 70° deposits monoclinic crystals, but of a different form from those of ferrous sulphate, $FeSO_4,7H_2O$—the angle of the prism being 71° 52′, that of the pinacoid, 95° 6′. This salt appears to be the same with 6 molecules of water as the tetragonal. Marignac also obtained magnesium and zinc salts with 6 molecules of water by evaporating their solutions at a higher temperature, and these salts were found to be isomorphous with the monoclinic nickel salt. In addition to this it must be observed that the rhombic crystals of nickel sulphate with $7H_2O$ become turbid under the influence of heat and light, lose water, and change into the tetragonal salt. The monoclinic crystals in time also become turbid, and change their structure, so that the tetragonal form of this salt is the most stable. We may also add that nickel sulphate in all its shapes forms very beautiful emerald-green crystals, which, when heated to 280°, assume a dirty greenish-yellow hue and then contain one molecule of water.

It may also be added that when equivalent aqueous solutions of NiX_2 (green) and CoX (red) are mixed together they give an almost colourless (grey) solution, in which the green and red colours of the component parts disappear owing to the combination of the complementary colours (Chap. XXI., note 28).

A double salt $NiKF_3$ is obtained by heating $NiCl_2$ with KFHF in a platinum crucible; $KCoF_3$ is formed in a similar manner. The nickel salt occurs in fine green plates, easily soluble in water, but scarcely at all in ethyl or methyl alcohol. They decompose into green oxide of nickel and potassium fluoride when heated in a current of air. The analogous salt of cobalt crystallises in crimson flakes.

Crystalline fluoride of nickel, NiF_2, obtained by heating the amorphous powder formed by decomposing the double ammonium salt in a stream of hydrofluoric acid, occurs in beautiful green prisms, sp. gr. 4·63, which are insoluble in water, alcohol, or ether; sulphuric, hydrochloric, and nitric acids also have no action upon them, even when heated; NiF_2 is decomposed by steam, with the formation of black oxide, which retains the crystalline structure of the salt. Fluoride of cobalt, CoF_2 (sp. gr. 4·4), resembles NiF_2, but fuses (1400°) with greater difficulty (Poulenc, 1892).

a **pink precipitate of cobaltous hydroxide,** Co(H_2O)$_2$, will be formed. If air be not completely excluded during the precipitation by boiling, the precipitate will also contain brown cobaltic hydroxide formed by the further oxidation of the cobaltous oxide.[34] Under similar circumstances nickel salts form **a green precipitate of nickelous hydroxide,** Ni(OH)$_2$, the formation of which is not hindered by the presence of ammonium salts, but in that case only requires more alkali to completely separate the nickel. The nickelous oxide obtained, either by heating the hydroxide, or from the carbonate or nitrate, is a grey powder, readily soluble in acids and easily reduced; but the same substance may be obtained in the crystalline form as an ordinary product from the ores; it crystallises in regular octahedra, with a metallic lustre, and is of a grey colour. In this state the nickelous oxide almost resists the action of acids.[34a]

It is interesting to note **the relation** of the cobaltous and nickelous hydroxides **to ammonia**; aqueous ammonia dissolves the precipitated cobaltous and nickelous hydroxides. The blue ammoniacal solution of nickel resembles a similar solution of cupric oxide, but has a somewhat reddish tint. It is characterised by the fact that it dissolves silk in

---

[34] Hydrated suboxide of cobalt (de Schulten, 1889) is obtained by heating a solution of $CoCl_2,6H_2O$ with caustic potash in a stream of coal gas. The hydrate which separates out dissolves in the caustic potash and forms a dark-blue solution. On leaving the solution to stand for 24 hours in atmosphere of coal gas (in order to prevent oxidation), Co(OH)$_2$ separates out as a violet powder, which is seen to be crystalline under the microscope. The specific gravity of this hydrate is 3·597 at 15°. It does not undergo change in the air; warm acetic acid dissolves it, but it is insoluble in either hot or cold solutions of ammonia and sal-ammoniac.

[34a] Potassium cyanide forms a precipitate with cobalt salts which is soluble in an excess of the reagent and forms a green solution. On heating this and adding a certain quantity of acid, a double **cobalt cyanide** is formed which corresponds with potassium ferricyanide. Its formation is accompanied with the evolution of hydrogen, and is founded upon the property which cobalt has of oxidising in an alkaline solution, the development of which has been observed in such a considerable measure in the cobaltamine salts (see note 85). The process which goes on here may be expressed as follows: $CoC_2N_2 + 4KCN$ first forms $CoK_4C_6N_6$, which salt with water, H_2O, forms potassium hydroxide, KHO, hydrogen, H, and the salt, $K_3CoC_6N_6$. Here naturally the presence of the acid is indispensable in consequence of its being required to combine with the alkali. From aqueous solutions this salt crystallises in transparent hexagonal prisms of a yellow colour, readily soluble in water. The reactions of double decomposition, and even the formation of the corresponding acid, are here exactly the same as in the case of the ferricyanide. If a nickelous salt be treated in precisely the same manner as that just described for a salt of cobalt, decomposition will occur. A similar relation is exhibited by CoX_2 in reacting with an excess of sodium nitrite, when $Na_3Co(NO_2)_6$ is formed in the solution (acidulated with acetic acid) and NO, proceeding from the oxidation of CoX_2 into CoX_3, is evolved. This sodium salt dissolves easily in water, but the corresponding potassium salt (also the Rb and Cs salts) are only slightly soluble (less so than the platinichlorides), so that sodium may be separated from potassium by this means. These double nitro-cobaltic salts are stable, and in general closely resemble the ferricyanides. Nickel does not form such compounds.

the same way as ammoniacal cupric oxide dissolves cellulose. Ammonia likewise dissolves the precipitate of cobaltous hydroxide, forming a brownish liquid, which becomes darker in air and finally assumes a bright-red hue, absorbing oxygen. The admixture of ammonium chloride prevents the precipitation of cobalt salts by ammonia; when the ammonia is added, a brown solution is obtained from which, as in the case of the preceding solution, potassium hydroxide does not separate the cobaltous oxide. Peculiar compounds are produced in this solution; they are comparatively stable, containing ammonia and an excess of oxygen; they bear the name cobaltoamine and cobaltiamine salts. They have been principally investigated by Genth, Frémy, Jörgensen, Werner, and others. Genth found that when a cobalt salt, mixed with an excess of ammonium chloride, is treated with ammonia and exposed to the air, after a certain lapse of time, on adding hydrochloric acid and boiling, a red powder is precipitated and the remaining solution contains an orange salt. The study of these compounds led to the discovery of a whole series of similar salts, some of which correspond with particular higher degrees of oxidation of cobalt, which are described later.[35]

---

[35] The cobalt salts may be divided into at least the following classes, which repeat themselves for Cr, Ir, Rh (we shall not stop to consider the latter, particularly as they closely resemble the cobalt salts), &c., and Jörgensen and Werner in 1897 and the neighbouring years added much to our knowledge of these complex compounds.

(*a*) **Ammonium cobalt salts,** which are simply direct compounds of the cobaltous salts, CoX_2, with ammonia, similar to various other compounds of the salts of silver, copper, and even calcium and magnesium, with ammonia. They are easily crystallised from an ammoniacal solution, and have a pink colour. Thus, for instance, when cobaltous chloride in solution is mixed with sufficient ammonia to redissolve the precipitate first formed, octahedral crystals are deposited which have a composition $CoCl_2,H_2O,6NH_3$. These salts are nothing else than combinations with ammonia of crystallisation—if it may be so termed—likening them in this way to combinations with water of crystallisation. This similarity is evident both from their composition and from their capability of giving off ammonia at various temperatures. The most important point to observe is that all these salts contain 6 molecules of ammonia to 1 atom of cobalt, and that this ammonia is held in fairly stable connection. Water decomposes these salts. (Nickel behaves similarly without forming other compounds corresponding to the true cobaltic.)

(*b*) The solutions of the above-mentioned salts are rendered turbid by the action of the air; they absorb oxygen and in strong solutions become covered with a crust of **oxycobaltamine salts.** The latter are sparingly soluble in aqueous ammonia, have a brown colour, and are characterised by the fact that with warm water **they evolve oxygen,** forming salts of the following category: The nitrate may be taken as an example of this kind of salt; its composition is $CoN_2O_7,5NH_3,H_2O$. It differs from cobaltous nitrate, $Co(NO_3)_2$, in containing an extra atom of oxygen—that is, it corresponds with cobalt dioxide, CoO_2, in the same way that the first salts correspond with cobaltous oxide; they contain 5, and not 6, molecules of ammonia, as if NH_3 had been replaced by O, but we shall afterwards meet compounds containing either $5NH_3$ or $6NH_3$ to each atom of cobalt.

(*c*) **The luteocobaltic salts** are thus called because they have a yellow (luteus) colour. They are obtained from the salts of the first kind by submitting them in dilute

Nickel does not possess this property of absorbing the oxygen of the air when in ammoniacal solution. In order to understand this distinc-

---

solution to the action of the air; in this case salts of the second kind are not formed, because they are decomposed by an excess of water, with the evolution of oxygen and the formation of luteocobaltic salts. By the action of ammonia the salts of the fifth kind (roseocobaltic) are also converted into luteocobaltic salts. These last-named salts generally crystallise readily, and have a yellow colour; they are comparatively much more stable than the preceding ones, and for a certain time resist even the action of boiling water. Boiling aqueous potash liberates ammonia and precipitates hydrated cobaltic oxide, $Co(OH)_2$, from them. This shows that the luteocobaltic salts correspond with cobaltic oxide, CoX_3, and those of the second kind with the dioxide. When a solution of luteocobaltic sulphate, $Co_2(SO_4)_3,12NH_3,4H_2O$, is treated with baryta, barium sulphate is precipitated, and the solution contains luteocobaltic hydroxide, $Co(OH)_3,6NH_3$, which is soluble in water, is powerfully alkaline, absorbs the oxygen of the air, and when heated is decomposed with the evolution of ammonia. The luteocobaltic salts again contain $6NH_3$ to each atom of cobalt, like the salts of the first kind. In the luteo-salts all the X's react (are ionised, as some chemists say) as in ordinary salts—for instance, all the Cl_3 is precipitated by a solution of $AgNO_3$; all the $(SO_4)_3$ gives a precipitate with BaX_2, &c. The double salt formed with $PtCl_4$ is composed in the same manner as the potassium salt (K_2PtCl_6), that is, it has the composition $(CoCl_3,6NH_3)_2,3PtCl_4$, the amount of chlorine in the $PtCl_4$ being double that in the alkaline salt.

In the rosepentamine (*e*), and rosetetramine (*f*), salts also, all the X's react or are ionised, but in the (*g*) and (*h*) salts only a portion of the X's react, and they are equal to the (*e*) and (*f*) salts minus water; this means that although the water dissolves them it is not combined with them, as PHO_3 differs from PH_3O_3; phenomena of this class correspond exactly to what has been already (Chap. XXI., note 7) mentioned respecting the green and violet salts of oxide of chromium.

(*d*) **The fuscocobaltic salts.**—An ammoniacal solution of cobalt salts acquires a brown colour in the air, due to the formation of these salts. They are also produced by the decomposition of salts of the second kind; they crystallise badly, and are separated from their solutions by addition of alcohol or an excess of ammonia. When boiled they give up the ammonia and cobaltic oxide which they contain. Hydrochloric and nitric acids give a yellow precipitate with these salts, which turns red when boiled, forming salts of the next category. The following formulæ represent the compositions of two of the fuscocobaltic salts: $Co_2O(SO_4)_2,8NH_3,4H_2O$ and $Co_2OCl_4,8NH_3,3H_2O$. It is evident that the fuscocobaltic salts correspond to the ammoniacal compounds of basic cobaltic salts. The normal cobaltic sulphate ought to have the composition $Co_2(SO_4)_3 = Co_2O_3,3SO_3$; the simplest basic salts will be $Co_2O(SO_4)_2 = Co_2O_3,2SO_3$, and $Co_2O_2(SO_4) = Co_2O_3,SO_3$. The fuscocobaltic salts correspond with the first type of basic salts. They are changed (in concentrated solutions) into oxycobaltamine salts by absorption of one atom of oxygen, $Co_2O_2(SO_4)_2$. Under many conditions the salts of fuscocobalt are easily transformed into salts of the next series. The salts of the series that has just been described contain 4 molecules of ammonia to 1 atom of cobalt.

(*e*) The **roseocobaltic** (or rosepentamine or aquapentaminocobaltic) **salts**, $CoX_2H_2O,5NH_3$, like the luteocobaltic, correspond to CoX_3, but contain less ammonia, and an extra molecule of water. Thus the sulphate is obtained from cobaltous sulphate dissolved in ammonia and left exposed to the air until transformed into a brown solution of the fuscocobaltic salt; when this is treated with sulphuric acid a crystalline powder of the roseocobaltic salt, $Co_2(SO_4)_3,10NH_3,5H_2O$, separates. This salt forms tetragonal crystals of a red colour, only slightly soluble in cold, but readily in warm water. When the sulphate is treated with baryta, roseocobaltic hydroxide is formed in the solution, which absorbs the carbonic anhydride of the air. It is obtained from the next series by the action of alkalies.

(*f*) The **rosetetramine cobaltic salts**, $CoCl_2,2H_2O,4NH_3$, were obtained by Jörgensen, and belong to the type of the luteo-salts, only with the substitution of $2NH_3$ for H_2O, tion, and in general the relation of nickel, it is important to observe that cobalt more easily forms a higher degree of oxidation—namely,

Like the luteo- and roseo-salts they give double salts with $PtCl_4$, similar to the alkaline double salts, for instance, $(Co,2H_2O,4NH_3)2(SO_4)_2Cl_2,PtCl_4$. They are darker in colour than the preceding, but also crystallise well. They are formed by dissolving $CoCO_3$ in sulphuric acid (of a given strength), and after NH_3 and carbonate of ammonium have been added, air is passed through the solution (for oxidation) until the latter turns red. It is then evaporated with lumps of carbonate of ammonium, filtered from the precipitate, and crystallised. A salt of the composition $Co_2(CO_3)_2(SO_4),(2H_2O,4NH_3)_2$ is thus obtained, from which the other salts may be easily prepared.

(*g*) The **purpureocobaltic salts** (pentamine), $CoX_3,5NH_3$, are also products of the direct oxidation of ammoniacal solutions of cobalt salts. They are easily obtained by heating the roseocobaltic and luteo-salts with strong acids. They are to all effect the same as the roseocobaltic salts, only anhydrous. Thus, for instance, the purpureocobaltic chloride, $Co_2Cl_6,10NH_3$, or $CoCl_3,5NH_3$, is obtained by boiling the oxycobaltamine salts with ammonia. There is the same distinction between these salts and the preceding ones as between the various compounds of cobaltous chloride with water. In the purpureocobaltic only X_2 out of the X_3 react (are ionised). To the rocetetramine salts (*f*) there correspond the **purpureotetramine** salts, $CoX_3H_2O,4NH_3$. The corresponding chromium purpureopentamine salt, $CrCl_3,5NH_3$ is obtained with particular ease (Christensen, 1898). Dry anhydrous chromium chloride is treated with anhydrous liquid ammonia in a freezing mixture composed of liquid CO_2 and chlorine, and after some time the mixture is taken out of the freezing mixture, so that the excess of NH_3 boils away; the violet crystals then immediately acquire the red colour of the salt, $CrCl_3,5NH_3$, which is formed. The product is washed with water (to extract the luteo-salt, $CrCl_3,6NH_3$), which does not dissolve the salt, and it is then recrystallised from a hot solution of hydrochloric acid.

(*h*) The **praseocobaltic salts**, $CoX_3,4NH_3$, are green, and form, with respect to the rosetetramine salts (*f*), the products of ultimate dehydration (for example, like metaphosphoric acid with respect to orthophosphoric acid), but in dissolving in water they give neither rosetetramine nor tetramine salts. (In my opinion one should expect salts with a still smaller amount of NH_3, but with H_2O and having the blue colour proper to the low-hydrated compounds of cobalt; the green colour of the praseo-salts already forms a step towards the blue). Jörgensen obtained salts for ethylene-diamine, $N_2H_4C_2H_4$, which replaces $2NH_3$. After being kept a long time in aqueous solution they give rosetetramine salts, just as metaphosphoric acid gives orthophosphoric acid, while the rosetetramine salts are converted into praseo-salts by Ag_2O and NaHO. Here only one X is ionised out of the X_3. There are also basic salts of the same type; but the best known is the chromium salt called the rhodozochromic salt, $Cr_2(OH)_3Cl_3,6NH_3,2H_2O$, which is formed by the prolonged action of water upon the corresponding roseo-salt.

The ammonio-metallic salts present a most complete qualitative and quantitative **resemblance to the hydrated salts of metals.** The composition of the latter is MX_n,mH_2O, where M = metal, X = the haloid, simple or complex, and n and m the quantities of the haloid and so-called water of crystallisation respectively. The composition of the ammoniacal salts of metals is MX_n,mNH_3. The water of crystallisation is held by the salt with more or less stability, and some salts even do not retain it at all; some part with water easily when exposed to the air, others when heated, and then only with difficulty. In the case of some metals all the salts combine with water, whilst with others only a few, and the water so combined may then be easily disengaged. All this applies equally well to the ammoniacal salts, and therefore the combined ammonia may be termed **the ammonia of crystallisation.** Just as the water which is combined with a salt is held by it with different degrees of force, so it is with ammonia. In combining with $2NH_3$, $PtCl_2$ evolves 81,000 cals.; while $CaCl_2$ only evolves 14,000 cals.; and the former compound parts with its NH_3 (together with HCl in this case) with more difficulty and only above 200°, while the latter disengages ammonia at 180°. The amount sesquioxide of cobalt, **cobaltic oxide**, Co_2O_3—than nickel, especially in the presence of hypochlorous acid. If a solution of a cobalt salt be

of combined ammonia is as variable as the amount of water of crystallisation; for instance, $SnI_4,8NH_3$; $CrCl_2,8NH_3$; $CrCl_3,6NH_3$; $CrCl_3,5NH_3$; $PtCl_2,4NH_3$; &c., are known. Very often NH_3 is replaceable by OH_2 and conversely. A colourless anhydrous cupric salt—for instance, cupric sulphate—forms blue and green salts when combined with water, and violet when combined with ammonia. If steam is passed through anhydrous copper sulphate the salt absorbs water and becomes heated; if ammonia is substituted for the water the heating becomes much more intense, and the salt breaks up into a fine violet powder. With water, $CuSO_4,5H_2O$ is formed, and with ammonia $CuSO_4,5NH_3$, the number of water and ammonia molecules retained by the salt being the same in each case, and as a proof of this, and that it is not an isolated coincidence, the remarkable fact must be borne in mind that water and ammonia consecutively, molecule for molecule, are capable of supplanting each other, and forming the compounds $CuSO_4,5H_2O$; $CuSO_4,4H_2O,NH_3$; $CuSO_4,3H_2O,2NH_3$; $CuSO_4,2H_2O,3NH_3$ $CuSO_4,H_2O,4NH_3$, and $CuSO_4,5NH_3$. The last of these compounds was obtained by Heinrich Rose, and my experiments have shown that more ammonia than this cannot be retained. By adding to a strong solution of cupric sulphate sufficient ammonia to dissolve the whole of the oxide precipitated, and then adding alcohol, Berzelius obtained the compound $CuSO_4,H_2O,4NH_3$, &c. The law of substitution also assists in rendering these phenomena clearer, because a compound of ammonia with water forms ammonium hydroxide, NH_4HO, and therefore these molecules combining with one another may also interchange, as being of equal value. And as ammonia is capable of combining with acids, and as some of the salts formed by slightly energetic bases in their properties more closely resemble acids (that is, salts of hydrogen) than others, we might expect to find more stable and more easily formed ammonio-metallic salts with metals and their oxides, having weaker basic properties than with those which form energetic bases. This explains why the salts of potassium, barium, &c., do not form ammonio-metallic salts, whilst the salts of silver, copper, zinc, &c., easily form them, and the salts RX_3 still more easily and with greater stability. This consideration also accounts for the great stability of the ammoniacal compounds of cupric oxide compared with those of silver oxide, since the former is displaced by the latter. It also enables us to see clearly the distinction which exists between the stability of the cobaltamine salts containing salts corresponding with cobaltous oxide, and that of those corresponding with higher oxides of cobalt, for the latter are weaker bases than cobaltous oxides. *The nature of the forces and quality of the phenomena occurring during the formation of the most stable substances, and of such compounds as crystallisable compounds, are one and the same, although perhaps exhibited in a different degree.* This, in my opinion, may be best confirmed by examining the compounds of carbon, because for this element the nature of the forces acting during the formation of its compounds is well known. Let us take as an example two unstable compounds of carbon. Acetic acid, $C_2H_4O_2$ (specific gravity 1·06), forms with water the hydrate, $C_2H_4O_2,H_2O$, denser (1·07) than either of the components, but unstable and easily decomposed, and generally simply referred to as a solution. Such also is the crystalline compound of oxalic acid, $C_2H_2O_4$, with water, $C_2H_2O_4,2H_2O$. Their formation might be predicted as starting from the hydrocarbon C_2H_6, in which, as in any other, the hydrogen may be exchanged for chlorine, the water residue (hydroxyl), &c. The first substitution product with hydroxyl, $C_2H_5(HO)$, is stable; it can be distilled without alteration, resists a temperature higher than 100°, and then does not give off water. This is ordinary alcohol. The second, $C_2H_4(HO)_2$, can also be distilled without change, but can be decomposed into water and C_2H_4O (ethylene oxide or aldehyde); it boils at about 197°, whilst the first hydrate boils at 78°, a difference of about 100°. The compound $C_2H_3(HO)_3$ will be the third product of such substitution; it ought to boil at about 300°, but does not resist this temperature—it decomposes into H_2O and $C_2H_4O_2$. The above-mentioned hydrate of acetic acid is such a decomposable hydrate—that is to say, what is called a solution. Still less stability mixed with barium carbonate and an excess of hypochlorous acid be added, or chlorine gas be passed through it, then at the ordinary

---

may be expected from the following hydrates forming glycollic, $C_2H_4O_3$, and glyoxylic, $C_2H_4O_4$, acids. The last hydrate, which ought to be obtained from C_2H_6, and ought to have the composition $C_2(HO)_6$, is the crystalline compound of oxalic acid, $C_2H_2O_4$ (two hydroxyl groups), and water, $2H_2O$, which has been already mentioned. The hydrate $C_2(HO)_6 = C_2H_2O_4,2H_2O$, ought, according to the foregoing reasoning, to boil at about 600°, but it does not resist this temperature, but at a much lower point splits up into water, $2H_2O$, and the hydrate $C_2O_2(HO)_2$, which is also capable of yielding water. Without going into further discussion of this subject, it may be observed that the formation of the hydrates, or compounds with water of crystallisation, of acetic and oxalic acids has thus received an accurate explanation, illustrating the point we desired to prove in affirming that compounds with water of crystallisation are held together by the same forces as those which act in the formation of other complex substances, and that the easy displaceability of the water of crystallisation is only a peculiarity of a local character, and not a radical point of distinction. Hence the forces which induce salts to combine with nH_2O or with nNH_3 are undoubtedly of the same order as the forces which govern the formation of ordinary 'atomic' and saline compounds. [A great impediment in the study of the former was caused by the conviction which reigned in the sixties and seventies, that 'atomic' were essentially different from 'molecular' compounds like crystallohydrates, in which it was assumed that there was a combination of entire molecules, as though without the participation of the atomic forces.] If the bonds between chlorine and different metals are not equally strong, so also the bond uniting nH_2O and nNH_3 is exceedingly variable; there is nothing very surprising in this. And in the fact that the combination of different amounts of NH_3 and H_2O alters the capacity of the haloids X of the salts RX_3 for reaction (for instance, in the luteo-salts all the X_3, while in the purpureo-, only 2 out of the 3, and in the praseo-salts only 1 of the 3 X's reacts), we should see, above all, a phenomenon similar to that known for many complex compounds, for organic compounds and for Cr_2Cl_6 (Chap. XXI., note 7a), for in both instances the essence of the difference lies in the removal of water; a molecule $RCl_3,6H_2O$ or $RCl_3,6NH_3$ contains the halogen in a perfectly mobile (ionised) state, while in the molecule $RCl_3,5H_2O$ or $RCl_3,5NH_3$ a portion of the halogen has almost lost its faculty for reacting with $AgNO_3$, just as metalepsical chlorine has lost this faculty which is fully developed in the chloranhydride. Until the reason of this difference be clear, we cannot expect that ordinary points of view and generalisation can give a clear answer. However, we may assume that the explanation here lies in the nature and kind of motion of the atoms in the molecules, although as yet it is not clear how. Nevertheless, I think it well to call attention again (Chap. I.) to the fact that the combination of water, and hence, also, of any other element, leads to most diverse consequences; the water in the gelatinous hydrate of alumina or in the decahydrated Glauber's salt is very mobile, and easily reacts like water in a free state; but the same water combined with oxide of calcium, or C_2H_4 (for instance, in C_2H_6O and in $C_4H_{10}O$), or with P_2O_5, has become quite different, and no longer acts like water in a free state. The chlorine in chlorates no longer gives a precipitate of chloride of silver with $AgNO_3$. Thus, although the instance which is found in the difference between the roseo- and purpureo-salts deserves to be fully studied on account of its simplicity, still it is far from being exceptional, and we cannot expect it to be thoroughly explained unless a mass of similar instances, which are exceedingly common among chemical compounds, be conjointly explained.

Kournakoff (1894) showed that at 0° the solubility of the luteo-salt, $CoCl_3,6NH_3$, is 4·80 (per 100 of water), and at 20°, 7·7; that in passing into the roseo-salt, $CoCl_3,H_2O,5NH_3$, the solubility rises considerably, and at 0° is 16·4, and at 20°, about 27, whilst the passage into the purpureo-salt, $CoCl_3,5NH_3$, is accompanied by a great fall in the solubility, which then has the value 0·23 at 0° and about 0·5 at 20°. And as crystallohydrates with a smaller amount of water are usually more soluble than the higher crystallohydrates (Le Chatelier), whilst here we find that the solubility falls (in the purpureo-salt) with a loss temperature, the whole of the cobalt will be separated, on shaking, in the form of black cobaltic oxide: $2CoSO_4+ClHO+2BaCO_3=Co_2O_3+2BaSO_4+HCl+2CO_2$. Under these circumstances, nickelous oxide does not immediately form black sesquioxide, but after a considerable space of time it also separates in the form of sesquioxide, Ni_2O_3, but always later than with cobalt, which shows the relative difficulty of further oxidation of the nickelous oxide. It is, however, possible to oxidise it; if, for instance, the hydroxide, NiH_2O_2, be shaken in water and chlorine gas be passed through it, then nickel chloride, which is soluble in water, will be formed, together with insoluble nickelic oxide in the form of a black precipitate: $3NiH_2O_2+Cl_2=NiCl_2+Ni_2O_3,3H_2O$. Nickelic oxide may also be obtained by adding sodium hypochlorite mixed with alkali to a solution of a nickel salt. Nickelic and cobaltic hydrates are black. Nickelic oxide evolves oxygen with all acids, and in consequence of this is not separated as a precipitate in the presence of acids; thus, it evolves chlorine with hydrochloric acid, exactly like manganese dioxide. When nickelic oxide is dissolved in aqueous ammonia it liberates nitrogen, and ammoniacal solution of nickelous oxide is formed. When heated, nickelic oxide loses oxygen, forming nickelous oxide. Cobaltic oxide, Co_2O_3, exhibits more stability than nickelic oxide, and shows feeble basic properties; it is dissolved by acetic acid without the evolution of oxygen.[35a] But ordinary acids, especially on heating, evolve oxygen, forming a solution of a cobaltous salt. The presence of a cobaltic salt in a solution of a cobaltous salt may be detected by the brown colour of the solution and the black precipitate formed by the addition of alkali, and also from the fact that such solutions evolve chlorine when heated with hydrochloric acid. Cobaltic oxide may be prepared not only by the above-mentioned methods, but also by heating cobalt nitrate, after which a steel-coloured mass remains which retains traces of nitric acid, but when further heated to incandescence evolves oxygen, leaving a compound of cobaltic and cobaltous oxides, similar to magnetic ironstone. Cobalt (but not nickel) undoubtedly forms, besides Co_2O_3, a **dioxide**, CoO_2. This is obtained[36]

---

of water, it follows that the water contained in the roseo-salt cannot be compared with water of crystallisation. Kournakoff, therefore, connects the fall in solubility (in the passage of the roseo- into the purpureo-salts) with the accompanying loss in the reactive capacity of the chlorine.

[35a] Marshall (1891) obtained cobaltic sulphate, $Co_2(SO_4)_3,18H_2O$, by the action of an electric current upon a strong solution of $CoSO_4$.

[36] According to Schroeder and Carnot, the precipitate produced by the hypochlorites has a composition $Co_{10}O_{16}$, whilst the oxide given by iodine in the presence of an alkali contains a larger amount of oxygen. Vortmann (1891) reinvestigated the composition of the higher oxygen oxide obtained by iodine in the presence of alkali, and found that the greenish precipitate (which disengages oxygen even when heated to only 100°)

when the cobaltous oxide is oxidised by iodine or peroxide of barium.[37]

Nickel alloys possess qualities which render them valuable for technical purposes, the alloy of nickel with iron being particularly remarkable. This alloy is met with in nature as **meteoric iron.** The Pallasoffsky mass of meteoric iron, preserved in the St. Petersburg Academy, fell in Siberia in the last century ; it weighs about 15 cwt. and contains 88 per cent. of iron, about 10 of nickel, together with a small admixture of other metals. The addition of a small amount of Ni to iron and steel increases their strength and elasticity, so that nickel steel containing up to 8 per cent. (but not more than 10 per cent.) of Ni is frequently used for making armour plates, and for other purposes. The alloys of Fe and Ni have acquired great theoretical and practical interest since Guillaume (1898) carried on his systematic researches at the Bureau of Weights and Measures (at Breteuil, near Paris) on these alloys, more especially on the coefficient of expansion and the capacity for magnetism. He found that the alloy containing about 28 per cent. Ni (probably $NiFe_3$, requiring 26·0 per cent. Ni) does not become magnetised. But what is still more remarkable is that the alloys containing about 35 per cent. of Ni (probably $NiFe_2$, which contains 34·5 per cent. of Ni) have exceedingly small coefficients of linear expansions (per 1° C.), namely, about 0·000,000,90, that is, less than that of the alloy containing 10 per cent. of iridium and 90 of platinum, which has the value 0·000,008,67, or those of iron or steel (0·000,010,46), nickel (0·000,012,65) and most metals.[37a] This property of the alloy

---

corresponds to the formula CoO_2. The reaction must be expressed by the equation: $CoX_2 + I_2 + 4KHO = CoO_2 + 2KX + 2KI + 2H_2O$.

[37] Prior to Vortmann, Rousseau (1889) endeavoured to solve the question as to whether CoO_2 was able to combine with bases and obtained $2(CoO_2)BaO$ and $CoO_2,BaO = BaO_2,CoO$, by breaking up the mass as it agglomerates together, and bringing the pieces into contact with the more heated surface of the crucible. This salt is formed between the somewhat narrow limits of temperature 1000°–1100°; above and below these limits compounds richer or poorer in CoO_2 are formed. The formation of CoO_2 by the action of BaO_2, and the easy decomposition of CoO_2 with the evolution of oxygen, give reason for thinking that it belongs to the class of peroxides (like Cr_2O_7, CaO_2, &c.); it is not yet known whether they give peroxide of hydrogen like the true peroxides. The fact that it is obtained by means of iodine (probably through HIO), coupled with its great resemblance to MnO_2, leads rather to the supposition that CoO_2 is a very feeble saline oxide. The form CoO_2 is repeated in the cobaltic compounds (note 35), and the existence of CoO_2 should have long ago been recognised upon this basis.

[37a] From a private communication I hear that Mons. Guillaume (September 1902) subsequently obtained the same 'invar' in such a state (whether by treatment or the addition of some substance to it, I do not know) that it does not expand when heated, but slightly contracts. All the above data hold good within the limits of 0° and 30°, but not for higher temperatures, when the structure of the metal and therefore the coefficient of expansion may vary.

approximating to $NiFe_2$ (it is called 'invar') renders it valuable for many scientific purposes, such as the preparation of standard measures of length, pendulums, &c., especially as it is very homogeneous, has a fine appearance, and is easily marked and polished. The alloys of Ni and Cu, containing a considerable proportion of Ni, are also silver white and just as suitable for making many scientific instruments, as they do not rust and take a very fine polish, which is essential for the inscription of micrometers, &c. In the arts, **german silver** is most extensively used ; this is an alloy containing nickel, copper, and zinc in various proportions. It generally consists of about 50 per cent. of copper, 25 of zinc, and 25 of nickel. This alloy is white like silver, and does not rust, and therefore furnishes an excellent substitute for silver in the majority of cases where it is used. Alloys which contain silver in addition to nickel show the properties of silver to a still greater extent. Alloys of nickel are used for coinage, and if rich deposits of nickel are discovered a wide field of application lies before it, not only in a pure state (because it is a beautiful metal and does not rust), but also for use in alloys.[37b]

Until 1890 no compound of cobalt or nickel was known of sufficient volatility to determine the molecular weights of the compounds of these metals ; but in 1890 L. Mond, in conducting (together with Langer and Quincke) his researches on the action of nickel upon carbonic oxide (Chap. IX., note 24a), observed that nickel gradually volatilises in a stream of carbonic oxide ; this only takes place at low temperatures, and is seen by the coloration of the flame of the carbonic oxide. This observation led to the discovery of a remarkable volatile **compound of nickel and carbonic oxide**, having the molecular composition $Ni(CO)_4$,[38]

[37b] The salts of nickel are poisonous, like those of copper and silver, but like Ag, Ni oxidises with difficulty and does not form salts under ordinary conditions, while Cu forms salts with great ease.

[38] This compound is known as nickel tetra-carbonyl. It appears to me as yet premature to judge of the structure of such an extraordinary compound as $Ni(CO)_4$. It has long been known that potassium combines with CO, forming $K_n(CO)_n$ (Chap. IX., note 31), but this substance is apparently saline and non-volatile, and has as little in common with $Ni(CO)_4$ as NaH has with SbH_3. However, Berthelot observed that when NiC_4N_4 is kept in air, it oxidises, and gives a colourless compound, $Ni_3C_2O_3,10H_2O$, having apparently saline properties. We may add that Schutzenberger, on reducing $NiCl_2$ by heating it in a current of hydrogen, observed that a nickel compound partly volatilises with the HCl and gives metallic nickel when heated again. The platinum compound, $PtCl_2(CO)_2$ (Chap. XXIII., note 11), offers the greatest analogy to $Ni(CO)_4$. This compound was obtained as a volatile substance by Schutzenberger (1868) by moderately heating (to 235°) metallic platinum in a mixture of chlorine and carbonic oxide. If we designate CO by Y, and an atom of chlorine by X, then, taking into account that, according to the periodic system, Ni is an analogue of Pt, a certain degree of correspondence is seen between the compositions NiY_4 and PtX_2Y_2. It would be interesting to compare the reactions of the two compounds.

as determined by the vapour density and by the depression of freezing-point. Cobalt and many other metals do not form volatile compounds under these conditions, but iron gives a similar product (note 26a). $Ni(CO)_4$ is prepared by taking finely divided Ni (obtained by reducing NiO by heating it in a stream of hydrogen, or by igniting the oxalate, NiC_2O_4)[39] and passing (at a temperature below 50°, for even at 60° decomposition may take place accompanied by an explosion) a stream of CO over it; the latter carries over the vapour of the compound, which condenses (in a well-cooled receiver) into a perfectly colourless, extremely mobile liquid, of sp. gr. 1·356 at 0°, boiling without decomposition at 43°, and crystallising in needles at —25°; it is insoluble in water, but soluble in alcohol and benzene, and burns with a very smoky flame (due to the liberation of Ni). When passed through a tube heated to 180° and above, the vapour deposits a brilliant coating of metal, and disengages CO. If the tube is strongly heated the decomposition is accompanied by an explosion. If $Ni(CO)_4$ as vapour is passed through a solution of $CuCl_2$, it reduces the latter to metal; it has the same action upon an ammoniacal solution of AgCl. Strong nitric acid oxidises $Ni(CO)_4$, but dilute solutions of acids have no action; if the vapour is passed through strong sulphuric acid, CO is liberated, while with chlorine it gives $NiCl_2$ and $COCl_2$; no simple reactions of double decomposition are yet known for $Ni(CO)_4$, however, so that its connection with other carbon compounds is not clear.[40]

---

[39] According to its empirical formula, anhydrous oxalate of nickel, NiC_2O_4, contains nickel and $2CO_2$.

[40] The following are the thermo-chemical data (according to Thomsen, and referred to gram weights expressed by the formula, in large calories or thousands of heat units) for the formation of corresponding compounds of Mn, Fe, Co, Ni, and Cu (+ Aq signifies that the reaction proceeds in an excess of water):

	R = Mn	Fe	Co	Ni	Cu
$R+Cl_2+Aq$	128	100	95	94	63
$R+Br_2+Aq$	106	78	73	72	41
$R+I_2+Aq$	76	48	43	41	32
$R+O+H_2O$	95	68	63	61	38
$R+O_2+SO_2+nH_2O$	193	169	163	163	130
RCl_2+Aq	+16	18	18	19	11

These examples show that for analogous reactions the amount of heat evolved in passing from Mn to Fe, Co, Ni, and Cu varies in regular sequence as the atomic weight increases. A similar difference is to be found in other groups and series, and proves that thermo-chemical phenomena are subject to the periodic law. It is most remarkable that Co and Ni give almost the same quantities of heat and have almost the same atomic weights.

CHAPTER XXIII

THE PLATINUM METALS

THE six metals : ruthenium, Ru, rhodium, Rh, palladium, Pd, osmium, Os, iridium, Ir, and platinum, Pt, are met with in nature associated together. Platinum always predominates over the others, and hence they are known as the **platinum metals**. By their chemical character their position in the periodic system is in the eighth group, corresponding with iron, cobalt, and nickel.

The natural transition from titanium and vanadium to copper and zinc by means of the elements of the iron group is demonstrated by all the properties of these elements, and in exactly the same manner a transition fron zirconium, niobium, and molybdenum to silver, cadmium, and indium, through ruthenium, rhodium, and palladium, is in perfect accordance with their properties and with the magnitude of the atomic weights, as also is the position of osmium, iridium, and platinum between tantalum and tungsten on the one side, and gold and mercury on the other. In all these three cases the elements of smaller atomic weight (chromium, molybdenum, and tungsten) are able, in their higher grades of oxidation, to give acid oxides having the properties of distinct but feebly energetic acids (in the lower oxides they give bases), whilst the elements of greater atomic weight (zinc, cadmium, mercury), even in their higher grades of oxidation, only give bases, and then only rather feeble ones. The platinum metals in forming comparatively feeble oxides with oxygen present the same intermediate properties as we have already seen in iron and the elements of the eighth group.

In the platinum metals the intermediate properties of **feebly acid and feebly basic metals** are developed with great clearness, so that there is not one sharply defined acid anhydride among their oxides, although there is a great diversity in the grades of oxidation, varying from the type RO_4 to R_2O. The feebleness of the chemical forces observed in the platinum metals is connected with the ready decomposability of their compounds. The oxides of platinum, iridium, and osmium can scarcely be termed either basic or acid; they are capable of combinations of both kinds, each of which is feeble, i.e., they are intermediate oxides.

The atomic weights of platinum, iridium, and osmium are about 191 to 196, and those of palladium, rhodium, and ruthenium, 104 to 106. Thus, strictly speaking, we have here two series of metals, which are, moreover, perfectly parallel to each other; three members in the first series, and three members in the second—platinum presents an analogy to palladium, iridium to rhodium, and osmium to ruthenium. As a matter of fact, however, the whole **group** of the platinum metals is characterised by **a number of common properties**, both physical and chemical, and, moreover, there are several points of resemblance between the members of this group and those of the **iron** group (Chap. XXII.). The atomic volumes of the elements of this group are **nearly equal** and **very small**. The iron metals have atomic volumes of about 7, whilst that of the metals allied to palladium is nearly 9, and of those adjacent to platinum (Pt, Ir, Os), nearly 9·4. This comparatively small atomic volume corresponds with the great infusibility and tenacity peculiar to all the iron and platinum metals, and to their small chemical energy, which stands out very clearly in the heavy platinum metals. All the platinum metals are very **easily reduced** by ignition and by the action of various reducing agents, in which process oxygen, or a haloid group, is disengaged from their compounds and the metal left behind. This is a property of the platinum metals which determines many of their reactions, and the circumstance of their always being found in nature **in a native state**. In Russia, in the Urals (discovered in 1819), and in Brazil (1735), platinum is obtained from alluvial deposits; but in 1892 Professor Inostrantseff discovered a vein deposit of platinum in serpentine near Tagil in the Urals.[1] Now almost all the platinum produced (about 6 tons a year) comes from the Urals.

The facility with which the platinum metals are reduced is so great that their chlorides are even decomposed by gaseous hydrogen, especially when shaken up and heated under a certain pressure. Hence it will be readily understood that such metals as zinc, iron, &c., separate them from solutions with great ease, this fact being taken advantage of in practice and in the chemical treatment of the platinum metals.[1a]

---

[1] Wells and Penfield (1888) have described a mineral, sperryllite, found in the Canadian gold-bearing quartz and consisting of platinum diarsenide, $PtAs_2$. It is a noticeable fact that this mineral clearly confirms the position of platinum in the same group as iron, because it corresponds in crystalline form (dodecahedra of the regular system) and chemical composition with iron pyrites, FeS_2.

[1a] Some light is thrown upon the facility with which the platinum compounds decompose, by Thomsen's data, which show that in an excess of water (+Aq) the formation from platinum of such a double salt as $PtCl_2,2KCl$, is accompanied by a comparatively small evolution of heat (see Chap. XXI., note 40), for instance, $Pt + Cl_2 + 2KCl + Aq$ only

All the platinum metals are grey, with a comparatively feeble metallic lustre, and are very infusible. In this respect they stand in the same order as the metals of the iron series; nickel is more fusible and whiter than cobalt and iron, and so also palladium is whiter and more fusible than rhodium and ruthenium, and platinum comparatively more fusible and whiter than iridium or osmium. The saline compounds of these metals are red or yellow. Moreover, certain complex compounds of the platinum metals, like certain complex compounds of the iron series, either have particular characteristic tints or are else colourless.

The platinum metals are found **in nature associated together in the alluvial deposits** of a few localities, from which they are washed, owing to their very considerable density, which enables a stream of water to remove the sand and clay with which they are mixed. Platinum deposits are known chiefly in the Urals, and also in Brazil and a few other localities. The platinum ore washed from these alluvial deposits presents the appearance of more or less coarse grains, and sometimes, as it were, of semi-fused nuggets.[2]

All the platinum metals give compounds with the halogens, and the highest haloid type of combination for all is RX_4. For the majority of the platinum metals this type is exceedingly unstable; the lower compounds, corresponding to the type RX_2, are more stable. In this type, RX_2, the platinum metals offer no little resemblance to the kindred compounds of the iron series—for example, to nickelous chloride, $NiCl_2$, cobaltous chloride, $CoCl_2$, &c. This even expresses itself in a similarity of volume (platinous chloride, $PtCl_2$, volume, 46; nickelous chloride, $NiCl_2$, 50), although in the type RX_2 the true iron metals give very stable compounds, whilst the platinum metals frequently react after the manner of suboxides, decomposing into the metal and higher types,

---

evolves about 33,000 calories (hence the reaction, $Pt + Cl_2 + Aq$, will evidently disengage still less, because $PtCl_2 + 2KCl$ evolves a certain amount of heat), whilst on the other hand, $Fe + Cl_2 + Aq$ gives 100,000 calories, and even the reaction with copper (for the formation of the double salt) evolves 63,000 calories.

[2] In the Urals a certain amount of gold is extracted from the washed platinum by means of mercury, which does not dissolve the platinum metals but dissolves the gold accompanying the platinum in its ores. The washed and mechanically sorted ore, in the majority of cases, contains about 70 to 80 per cent. of platinum, about 5 to 8 per cent. of iridium, and a somewhat smaller quantity of osmium. The other platinum metals—palladium, rhodium, and ruthenium—occur in smaller proportions than the above-named. Sometimes grains of almost pure osmium-iridium, containing only a small quantity of other metals, are found in platinum ores. This **osmium-iridium** may be easily separated from the other platinum metals, owing to its being nearly insoluble in aqua regia, by which the latter are easily dissolved. There are grains of platinum which are magnetic The grains of osmium-iridium are very hard and malleable, and are therefore used for certain purposes, for instance, for the tips of fountain pens.

$2RX_2 = R + RX_4$. This probably depends on the facility with which RX_2 decomposes into R and X_2, the latter then combining with the remaining portion of RX_2.

As in the series iron, cobalt, and nickel, nickel gives NiO and Ni_2O_3, whilst cobalt and iron give higher and varied forms of oxidation, so also among the platinum metals, platinum and palladium only give the forms RX_2 and RX_4, whilst rhodium and iridium form another and intermediate type, RX_3, also met with in cobalt, corresponding with the oxide having the composition R_2O_3, besides which they form an acid oxide, like ferric acid, which is also known in the form of salts, but is in every respect unstable. **Osmium** and **ruthenium**, like manganese, form still higher oxides, and in this respect exhibit the greatest diversity. They not only give RX_2, RX_3, RX_4, and RO_2X_2, but also a still **higher form of oxidation**, RO_4, which is not met with in any other series. This form is exceedingly characteristic, owing to the fact that the oxides, OsO_4 and RuO_4, are volatile and have feebly acid properties. In this respect they most resemble permanganic anhydride, which is also somewhat volatile.[3]

When dissolved in aqua regia ($PtCl_4$ is formed) and liberated from the solution by sal-ammoniac [$(NH_4)_2PtCl_6$ is formed] and reduced by ignition (which may be done by Zn and other reducing agents, directly from a solution of $PtCl_4$) platinum [3a] forms a powdery mass, known

---

[3] The platinum metals are capable of forming a sort of unstable compound with **hydrogen**; they absorb the gas and only part with it when somewhat strongly heated. This faculty is especially developed in platinum and palladium, and it is very characteristic that nickel, which exactly corresponds with platinum and palladium in the periodic system, should exhibit the same faculty for retaining a considerable quantity of hydrogen (Graham's and Raoult's experiments). Another characteristic property of the platinum metals consists in their easily giving (like cobalt, which forms the cobaltic salts) complex saline **compounds with ammonia**, and, like Fe and Co, double salts with the cyanides of the alkali metals, especially in their lower forms of combination.

[3a] Platinum was first obtained in the eighteenth century from Brazil, where it was called silver (*platinas*). Watson characterised platinum as a separate independent metal. In 1803 Wollaston discovered palladium and rhodium in crude platinum, and at about the same time Tennant distinguished iridium and osmium in it. Professor Claus, of Kazan, in his researches on the platinum metals (about 1840) discovered ruthenium in them, and to him are due many important discoveries with regard to these elements, including the indication of the remarkable analogy between the series Pd—Rh—Ru and Pt—Ir—Os.

The treatment of platinum ore is chiefly carried on for the extraction of the platinum itself and of its alloys with iridium, because these metals offer a greater resistance to the action of chemical reagents and high temperatures than any of the other malleable and ductile metals, and therefore the wire so often used in the laboratory and for technical purposes (especially in electro-technics) is made from them, as also are various vessels used for chemical purposes in the laboratory and in works. Thus sulphuric acid is distilled in platinum retorts, and many substances are fused, ignited, and evaporated in the laboratory in platinum crucibles and on platinum foil. Gold, &c., are as spongy platinum or platinum black. If this powder of platinum is heated and pressed, or hammered in a cylinder, the grains aggregate or forge together, and form a continuous, though not entirely homogeneous, mass. Platinum was formerly worked up in this manner. The platinum money formerly used in Russia was made in this way. Sainte-Claire Deville, in the fifties, for the first time **melted platinum** in considerable quantities by employing a special furnace made in the form of a small reverberatory furnace, and composed of two pieces of lime, on which the heat of the oxyhydrogen flame has no action. Into this furnace (shown in fig. 88, Vol. I., p. 172)—or, more strictly speaking, into the cavity made in the pieces of lime—the platinum is introduced, and two orifices are made in the lime; through one, the upper, or side orifice, is introduced an oxyhydrogen gas burner, in which either detonating gas or a mixture of oxygen and coal-gas is burnt, whilst the other orifice serves for the escape of the products of combustion and certain impurities which are more volatile than the platinum, and especially the oxidised compounds of osmium, ruthenium (and palladium), which are comparatively easily volatilised by heat. In this manner the platinum is converted into a homogeneous metallic form by means of fusion.[4]

To obtain pure platinum, the ore is treated with aqua regia in which only the osmium and iridium are insoluble. The solution contains the platinum metals in the form RCl_4, and in the lower forms of chlorina-

---

dissolved in dishes made of iridium-platinum, because the alloys of platinum and iridium are but slightly attacked when subjected to the action of aqua regia.

The comparatively high density (about 21·5), hardness—nearly that of steel (Pt is soft)—ductility, and infusibility (it does not melt at a furnace heat, but only in the oxyhydrogen flame or electric furnace), as well as the fact of its resisting the action of water, air, and other reagents, renders an alloy of 90 parts of platinum and 10 parts of iridium (Deville's platinum-iridium alloy) a most valuable material for making standard weights and measures, such as the metre, kilogram, and pound, and therefore all the newest standards of most countries are made of this alloy.

[4] This process has altered the technical treatment of platinum to a considerable extent. It has in particular facilitated the manufacture of alloys of platinum with iridium and rhodium from the pure platinum ores, since it is sufficient to fuse the ore in order for the greater amount of the osmium to burn off, and for the mass to fuse into a homogeneous malleable alloy, which can be directly made use of. There is very little ruthenium in the ores of platinum. If during fusion lead is added, it dissolves the platinum (and other platinum metals), owing to its being able to form a very characteristic alloy of the composition PtPb. If an alloy of the two metals is left exposed to moist air, the excess of lead is converted into carbonate (white lead) in the presence of the water and carbonic acid of the air, whilst the above platinum alloy remains unchanged. The white lead may be extracted by dilute acid, and the alloy PtPb remains unaltered. The fusibility of these alloys enables the platinum metals to be separated from the gangue of the ore, and they may afterwards be separated from the lead by subjecting the alloy to oxidation in furnaces furnished with a bone ash bed, because the lead is then oxidised and absorbed by the bone ash, leaving the platinum metals untouched (H. Sainte-Claire Deville, 1865).

tion, RCl_3 and RCl_2, because some of these metals—for instance, palladium and rhodium—form such unstable chlorides of the type RX_4 that they partially decompose even when diluted with water, and pass into the stable lower type of combination ; in addition to which, the chlorine is very easily disengaged if it comes into contact with substances on which it can act. In this respect platinum resists the action of heat and reducing agents better than any of its companions—that is, it passes with greater difficulty from $PtCl_4$ to the lower compound $PtCl_2$. On this is based the method of preparation of more or less pure platinum. Lime or sodium hydroxide is added to the solution in aqua regia until the liquid is neutralised or only contains a very slight excess of alkali. It is best to first evaporate and slightly ignite the solution, in order to remove the excess of acid, and by heating it to partially convert the higher chlorides of the palladium, &c., into the lower. The addition of alkalies completes the reduction, because the chlorine held in the compounds RX_4 acts on the alkali like free chlorine, converting it into a hypochlorite. Thus palladium chloride, $PdCl_4$, for example, is converted into palladous chloride, $PdCl_2$, by this means, according to the equation, $PdCl_4 + 2NaHO = PdCl_2 + NaCl + NaClO + H_2O$. In a similar manner iridic chloride, $IrCl_4$, is converted into the trichloride, $IrCl_3$, by this method. When this conversion takes place, the platinum still remains in the form of platinic chloride, $PtCl_4$. It is then possible to take advantage of a certain difference in the properties of the higher and lower chlorides of the platinum metals. Thus lime precipitates the lower chlorides of the members of the platinum metals occurring in solution without acting on the platinic chloride, $PtCl_4$, and hence the addition of a large proportion of lime immediately precipitates the associated metals, leaving the platinum itself in solution in the form of a soluble double salt, $PtCl_4,CaCl_2$. A far better and more perfect **separation** is effected **by means of ammonium chloride**, which gives, with platinic chloride, an insoluble yellow precipitate, $PtCl_4,2NH_4Cl$, whilst it forms soluble double salts with the lower chlorides RCl_2 and RCl_3, so that ammonium chloride precipitates the platinum only from the solution obtained by the preceding method. These methods are employed for preparing the platinum which is used for the manufacture of platinum articles, because, having platinum in solution as calcium platinichloride, $PtCaCl_6$, or as the insoluble ammonium platinichloride, $Pt(NH_4)_2Cl_6$, the platinum compound in every case, after drying or ignition, loses all the chlorine from the platinic chloride and leaves finely divided metallic platinum, which may be converted into homogeneous metal by compression and forging, or by fusion.[5]

---

[5] For the ultimate purification of platinum from palladium and iridium the metals

Metallic **platinum** in a fused state has a specific gravity of about 21; it is grey, softer than iron, but harder than copper, exceedingly ductile, and therefore easily drawn into wire and rolled into thin sheets, and may be hammered into crucibles and drawn into thin tubes, &c. In the state in which it is obtained by the ignition of its compounds, it forms a spongy mass, known as spongy platinum, or else as powder

---

must be re-dissolved in aqua regia, and the solution evaporated until the residue begins to evolve chlorine. The residue is then re-precipitated with ammonium or potassium chloride. The precipitate may still contain a certain amount of iridium, which passes with greater difficulty from the tetrachloride, $IrCl_4$, into the trichloride, $IrCl_3$; but it will be quite free from palladium, because the latter easily loses its chlorine and passes into palladious chloride, $PdCl_2$, which gives an easily soluble salt with potassium chloride. The precipitate, containing a small quantity of iridium, is then heated with sodium carbonate, giving metallic platinum and iridium oxide. If potassium chloride has been employed, the residue after ignition is washed with water and treated with aqua regia. The iridium oxide remains undissolved, and the platinum passes easily into solution. Only cold and dilute aqua regia must be used. The solution will then contain pure platinic chloride, which forms the starting-point for the preparation of all platinum compounds. The three following are very sensitive tests (to thousandths of a per cent.) for the presence of Ir, Ru, Rh, Pd (osmium is not usually present in platinum which has once been purified, since it easily volatilises with Cl_2 and CO_2, and in the first treatment of the crude platinum either passes off as OsO_4 or remains undissolved), Fe, Cu, Ag, and Pb: (1) the assay is alloyed with 10 parts of pure lead, the alloy treated with dilute nitric acid (to remove the greater part of the Pb), and dissolved in aqua regia; the residue will consist of Ir and Ru; the Pb is precipitated from the nitric acid solution by sulphuric acid, whilst the remaining platinum metals are reduced from the evaporated solution by formic acid, and the resultant precipitate fused with $KHSO_4$; the Pd and Rh are thus converted into soluble salts, and the former is then precipitated by HgC_2N_2. (2) Iron may be detected by the usual reagents, if the crude platinum be dissolved in aqua regia, and the platinum metals precipitated from the solution by formic acid. (3) If crude platinum (as foil or sponge) is heated in a mixture of chlorine and carbonic oxide, it volatilises (with a certain amount of Ir, Pd, Fe, &c.) as $PtCl_2,2CO$ (note 11), whilst the whole of the Rh, Ag, and Cu it may contain remains behind. Among other characteristic reactions for the platinum metals, we may mention: (1) that rhodium is precipitated from the solution obtained after fusion with $KHSO_4$ (in which Pt does not dissolve) by NH_3, acetic and formic acids; (2) that dilute aqua regia dissolves precipitated Pt, but not Rh; (3) that if the insoluble residue of the platinum metals (Ir, Ru, Os) obtained, after treating with aqua regia, be fused with a mixture of 1 part of KNO_3 and 3 parts of K_2CO_3 (in a gold crucible), and then treated with water, it gives a solution containing the Ru (and a portion of the Ir), but which throws it all down when saturated with chlorine and boiled; (4) that if iridium is fused with a mixture of KHO and KNO_3, it gives a soluble potassium salt, IrK_2O_4 (the solution is blue), and this, when saturated with chlorine, gives $IrCl_4$, which is precipitated by NH_4Cl (the precipitate is black), forming a double salt, leaving metallic Ir after ignition; (5) that rhodium mixed with NaCl and ignited in a current of chlorine gives a soluble double salt (from which sal-ammoniac separates Pt and Ir), which gives (according to Jörgensen) a difficultly soluble purpureo-salt (Chap. XXII., note 35), $Rh_2Cl_3,5NH_3$, when treated with NH_3; in this form the Rh may be easily purified and obtained as metal by igniting in hydrogen; and (6) that palladium, dissolved in aqua regia and dried (NH_4Cl throws down any Pt), gives soluble $PdCl_2$, which forms an easily crystallisable yellow salt, $PdCl_2NH_3$, with ammonia; this salt (Wilm) may be easily purified by crystallisation, and gives metallic Pd when ignited. These reactions illustrate the method of separating the platinum metals from each other.

(platinum black).[6] In either case it is dull-grey, and is characterised, as we already know, by the faculty of absorbing hydrogen and other gases. Platinum is not acted on by hydrochloric, hydriodic, nitric, and sulphuric acids, or by a mixture of hydrofluoric and nitric acids. Aqua regia, or any liquid containing chlorine or able to evolve chlorine or bromine, dissolves platinum. Alkalies are decomposed by platinum at a red heat, owing to the faculty of the platinum oxide, PtO_2, formed to combine with alkaline bases, inasmuch as it has a feebly developed acid character (see note 8). Sulphur, phosphorus (the phosphide, PtP_2, is formed), arsenic, silicon, and especially antimony, all act more or less rapidly on platinum, under the influence of heat. Many of the metals form alloys with it. Even charcoal combines with platinum when it is ignited with it, and therefore carbonaceous matter cannot be subjected to prolonged and powerful ignition in platinum vessels. Hence a platinum crucible soon becomes dull on the surface in a smoky flame. Platinum also forms alloys with zinc, lead, tin, antimony, copper, gold, and silver.[7] Although mercury does not directly dissolve platinum, still it forms a solution or amalgam with spongy platinum in the presence of sodium amalgam; a similar amalgam is also formed by the action of sodium amalgam on a solution of platinum chloride, and is used for physical experiments.

There are **two kinds of platinum compounds**, PtX_4 and PtX_2. The former are produced by an excess of halogen in the cold, and the

---

[6] We have already become acquainted with the effect of finely divided platinum on many gaseous substances. It is best seen in the so-called **platinum black**, which is a grey or black powder, left by the action of sulphuric acid on the alloy of zinc and platinum, or precipitated by metallic zinc from a dilute solution of platinum. In any case, finely divided platinum absorbs gases more powerfully and rapidly the more finely divided and porous it is. Sulphurous anhydride, hydrogen, alcohol, and many organic substances in the presence of such platinum are easily oxidised by the oxygen of the air, although they do not combine with it directly. The absorption of oxygen is as much as several hundred volumes per one of platinum, and the oxidising power of such absorbed oxygen is taken advantage of not only in the laboratory, but even in manufacturing processes. Asbestos or charcoal, soaked in a solution of platinic chloride and ignited, is very useful for this purpose, because by this means it becomes coated with platinum black (Chap. XX., note 48a). If 50 grams of $PtCl_4$ is dissolved in 60 c.c. of water, and 70 c.c. of a strong (40 p.c.) solution of formic aldehyde added, the mixture cooled, and then a solution of 50 grams of NaHO in 50 grams of water added, the platinum is precipitated. After washing with water the precipitate passes into solution and forms a black liquid containing *soluble colloidal platinum* (Loew, 1890). If the precipitated platinum be allowed to absorb oxygen on the filter, the temperature rises 40°, and a very porous *platinum black* is obtained which vigorously facilitates oxidation.

[7] It is necessary to remark that platinum when alloyed with silver, or as amalgam, is soluble in nitric acid, and in this respect it differs from gold, so that it is possible, by alloying gold with silver, and acting on the alloy with nitric acid, to recognise the presence of platinum in the gold, because nitric acid does not act on gold alloyed with silver.

latter by the aid of heat or by the splitting up of the former. The starting-point for the platinum compounds is **platinum tetrachloride, or platinic chloride,** $PtCl_4$, obtained by dissolving platinum in aqua regia.[7a] The solution crystallises in the cold, in a desiccator, in the form of reddish-brown deliquescent crystals which contain hydrochloric acid, $PtCl_4,2HCl,6H_2O$, and behave like a true acid whose salts correspond to the formula R_2PtCl_6—ammonium platinichloride, for example.[7b] The hydrochloric acid is liberated from the HCl compound by gently heating (or, better still, after treatment with silver nitrate), a reddish-brown mass remaining behind, yielding a yellowish-red solution which on cooling deposits crystals of the composition $PtCl_4,8H_2O$. The **tendency** of $PtCl_4$ **to combine** with hydrochloric acid and water —that is, **to form higher crystalline compounds**—is evident in all the platinum compounds, and must be taken into account in explaining the formation of many others of its complex compounds. Dilute solutions of platinic chloride are yellow, and are completely reduced by hydrogen, sulphurous anhydride, and many reducing agents, which first convert the platinic chloride into the lower compound, platinous chloride, $PtCl_2$. That faculty, which reveals itself in platinum tetrachloride, of combining with water of crystallisation and hydrochloric acid, is distinctly marked in its property, with which we are already acquainted, of giving precipitates with the salts of potassium, ammonium, rubidium, &c. In general it **readily forms double salts,** $R_2PtCl_6 = PtCl_4 + 2RCl$, where R is a univalent metal such as potassium or NH_4. Hence the addition of a solution of potassium or ammonium chloride to a solution of platinic chloride is followed by the formation of a yellow precipitate, which is sparingly soluble in water and almost entirely insoluble in alcohol and ether (platinic chloride is soluble in alcohol, potassium iridiochloride, IrK_3Cl_6, i.e., a compound of $IrCl_3$, being soluble in water but not in alcohol). It is especially remarkable in this case that here, as in many other instances, the potassium compounds separate in an anhydrous form, whilst the sodium compounds, which are soluble in water and alcohol, form red crystals containing water. The composition $Na_2PtCl_6,6H_2O$ exactly corresponds with the above-mentioned hydrochloric compound. The compounds

---

[7a] $PtCl_4$ is also formed by the action of a mixture of HCl vapour and air, and by the action of gaseous chlorine, upon platinum.

[7b] Pigeon (1891) obtained fine yellow crystals of $PtH_2Cl_6,4H_2O$ by adding strong sulphuric acid to a strong solution of $PtH_2Cl_6,6H_2O$. If crystals of $H_2PtCl_6,6H_2O$ are melted *in vacuo* (60°) in the presence of anhydrous potash, a red-brown solid hydrate is obtained containing less water and HCl, which parts with the remainder at 200°, leaving anhydrous $PtCl_4$. The latter does not disengage chlorine before 220°, and is perfectly soluble in water.

with barium, $BaPtCl_6,4H_2O$, strontium, $SrPtCl_6,8H_2O$, calcium, magnesium, iron, manganese, and many other metals are all soluble in water.[8]

Platinous chloride, $PtCl_2$, is formed when hydrogen platinichloride, PtH_2Cl_6, is ignited at 300°, or when platinum is heated at 230° in a stream of chlorine. The undecomposed tetrachloride is extracted from the residue by washing it with water, and a greenish-grey or brown insoluble mass of the dichloride (sp. gr. 5·9) is then obtained. It is soluble in hydrochloric acid, giving an acid solution of the composition $PtCl_2,2HCl$, corresponding with the type of double salts, PtR_2Cl_4. Although platinous chloride decomposes below 500°, it is still formed to a small extent at higher temperatures. Troost and Hautefeuille, and Seelheim observed that when platinum was strongly ignited in a stream of chlorine, the metal, as it were, slowly volatilised and was deposited in crystals; a volatile chloride, probably platinous chloride, was evidently formed in this case, and decomposed subsequently to its formation, depositing crystals of platinum.

The above-described properties of platinum are repeated more or less distinctly, or sometimes with certain modifications in the above-mentioned associates and analogues of this metal. Thus, although palladium

---

[8] Nilson (1877), who investigated the platinochlorides of various metals subsequently to Bonsdorff, Topsöe, Clève, Marignac, and others, found that univalent and bivalent metals—such as hydrogen, potassium, ammonium . . . beryllium, calcium, barium—give compounds of such a composition that there is always twice as much chlorine in the platinic chloride as in the combined metallic chloride; for example, $K_2Cl_2,PtCl_4$; $BeCl_2,PtCl_4,8H_2O$, &c. Such trivalent metals as aluminium, iron (ferric), chromium, didymium, and cerium (cerous) form compounds of the type $RCl_3,PtCl_4$, in which the amounts of chlorine are in the ratio 3 : 4. Only indium and yttrium give salts of a different composition—namely, $2InCl_3,5PtCl_4,36H_2O$ and $4YCl_3,5PtCl_4,51H_2O$. Such quadrivalent metals as thorium, tin, and zirconium give compounds of the type $RCl_4,PtCl_4$, in which the ratio of the chlorine is 1 : 1. In this manner the valency of a metal may, to a certain extent, be judged from the composition of the double salts formed with platinic chloride.

Platinic bromide, $PtBr_4$, and iodide, PtI_4, are analogous to the tetrachloride, but the iodide is decomposed still more easily than the chloride. If sulphuric acid is added to platinic chloride, and the solution evaporated, it forms a black porous mass like charcoal, which deliquesces in the air, and has the composition $Pt(SO_4)_2$. But this, the only oxygen salt of the type PtX_4, is exceedingly unstable. This is due to the fact that **platinum oxide**, the oxide of the type PtO_2, has a feeble acid character. This is shown in a number of instances. Thus, if a strong solution of platinic chloride treated with sodium carbonate be exposed to the action of light or evaporated to dryness and then washed with water, a sodium platinate, $Pt_3Na_2O_7,6H_2O$, remains. The composition of this salt, if we regard it in the same sense as we did the salts of silicic, titanic, molybdic, and other acids, will be $PtO(ONa)_2,2PtO_2,6H_2O$—that is, the same type is repeated as we saw in the crystalline compounds of platinum tetrachloride with sodium chloride, or with hydrochloric acid—namely, the type $PtX_4,8Y$, where Y is a molecule of H_2O, HCl, &c. Similar compounds are also obtained with other alkalies. They will be platinates of the alkalies in which the platinic oxide, PtO_2, plays the part of an acid oxide. Rousseau (1889) obtained different grades of combination BaO,PtO_2, $3(BaO),2PtO_2$, &c., by igniting a mixture of $PtCl_4$ and caustic baryta. If such an alkaline compound of platinum is forms $PdCl_4$, this form passes into $PdCl_2$ with extreme ease.[9] Whilst rhodium and iridium in dissolving in aqua regia also form $RhCl_4$ and

treated with acetic acid, the alkali combines with the latter, and a **platinic hydroxide**, $Pt(OH)_4$, remains as a brown mass, which loses water and oxygen when ignited, and in so doing decomposes with a slight explosion. When slightly ignited this hydroxide first loses water and gives the very unstable oxide, PtO_2. Platinic sulphide, PtS_2, belongs to the same type; it is precipitated by the action of sulphuretted hydrogen on a solution of platinum tetrachloride. The moist precipitate is capable of attracting oxygen, and is then converted into the sulphate above mentioned, which is soluble in water. This absorption of oxygen and conversion into sulphate is another illustration of the basic nature of PtO_2, so that it clearly exhibits both basic and acid properties. The latter appear, for instance, in the fact that platinic sulphide, PtS_2, gives crystalline compounds with the alkali sulphides.

[9] In comparing the characteristics of the platinum metals, it must be observed that palladium, in its form of combination PdX_2, gives saline compounds of considerable stability. Amongst them **palladous chloride** is formed by the direct action of chlorine or aqua regia (not in excess or in dilute solutions) on palladium. It forms a brown solution, which gives a black insoluble precipitate of **palladous iodide**, PdI_2, with solutions of iodides (in this respect, as in many others, palladium resembles mercury in the mercuric compounds, HgX_2). With a solution of mercuric cyanide it gives a yellowish-white precipitate, palladous cyanide, PdC_2N_2, which is soluble in potassium cyanide, and gives other double salts, $M_2PdC_4N_4$.

That portion of the platinum ore which dissolves in aqua regia and is precipitated by ammonium or potassium chloride does not contain palladium. It remains in solution, because the palladic chloride, $PdCl_4$, is decomposed and the palladous chloride formed is not precipitated by ammonium chloride; the same holds good for all the other lower chlorides of the platinum metals. Zinc (or iron) separates out all the unprecipitated platinum metals (and also copper, &c.) from the solution. The palladium is found in these 'platinum residues' precipitated by zinc. If this mixture of metals be treated with aqua regia, all the palladium will pass into solution as palladous chloride, together with some platinic chloride. By this treatment the main portion of the iridium, rhodium, &c., remains almost undissolved, the platinum is separated from the mixture of palladous and platinic chlorides by a solution of ammonium chloride, and the solution of palladium is precipitated by potassium iodide or mercuric cyanide. Wilm (1881) showed that palladium may be separated from an impure solution by saturating it with ammonia; all the iron present is thus precipitated, and, after filtering, the addition of hydrochloric acid to the filtrate gives a yellow precipitate of an ammonio-palladium compound, $PdCl_2,2NH_3$, whilst nearly all the other metals remain in solution. **Metallic palladium** is obtained by igniting the ammonio-compound or the cyanide, PdC_2N_2. It occurs native, although rarely, is a metal of a whiter colour than platinum, has the sp. gr. 11·4, and melts at about 1500°; it is much more volatile than platinum, and partially oxidises on the surface when heated. Wilm obtained spongy palladium by igniting $PdCl_2,2NH_3$, and observed that it gives PdO (together with Pd_2O, according to Ramsay) when ignited in oxygen, and that on further ignition this oxide forms a mixture of Pd_2O and Pd and loses its absorbed oxygen on a further rise of temperature. It does not blacken or tarnish (does not absorb sulphur) in the air at the ordinary temperature, and is therefore better suited than silver for astronomical and other instruments in which fine divisions have to be engraved on a white metal, in order that the fine lines should be clearly visible. The most remarkable property of palladium, discovered by Graham, consists in its capacity for **absorbing** a large amount of **hydrogen**. Ignited palladium absorbs as much as 940 volumes of hydrogen, or about 0·7 per cent. of its own weight, which closely approaches to the formation of the compound Pd_3H_2, and probably indicates the formation of **palladium hydride**, Pd_2H. This absorption also takes place at the ordinary temperature—for example, when palladium serves as an electrode at which hydrogen is evolved. In absorbing the hydrogen, the palladium does not change

$IrCl_4$, but these pass into $RhCl_3$ and $IrCl_3$[9a] very easily when heated or when acted upon by substances capable of taking up chlorine (even

---

in appearance, and retains all its metallic properties, but its volume increases about 10 per cent.—that is, the hydrogen pushes out and separates the atoms of the palladium from each other, and is itself compressed to $\frac{1}{900}$ of its volume. This compression indicates a great force of chemical attraction, and is accompanied by the evolution of heat (Chap. II., note 38). The absorption of 1 grm. of hydrogen by metallic palladium (Favre) is accompanied by the evolution of 4·2 thousand calories (for Pt, 20; for Na, 13; for K, 10 thousand units of heat). Troost showed that the dissociation pressure of palladium hydride is inconsiderable at the ordinary temperature, but reaches the atmospheric pressure at about 140°. All the hydrogen passes off at 440°. This subject was subsequently investigated by A. A. Cracow (1894), who showed that at first the absorption of hydrogen by the palladium proceeds like solution, according to the law of Dalton and Henry, but that towards the end it proceeds like a dissociation phenomenon in definite compounds; this forms another link between the phenomenon of solution and that of the formation of definite atomic compounds.

The absorbed hydrogen is easily disengaged by ignition or decreased pressure. The resultant compound does not decompose at the ordinary temperature, but when exposed to air the metal sometimes glows spontaneously, owing to the hydrogen burning at the expense of the atmospheric oxygen. The hydrogen absorbed by palladium acts towards many solutions as a reducing agent; in a word, everything here points to the formation of a definite compound and at the same time of a physically compressed gas, and forms one of the best examples of the bond existing between chemical and physical processes, to which we have many times drawn attention. It must be again remembered that the other metals of the eighth group, even copper, are, like palladium and platinum, able to combine with hydrogen. The permeability of iron and platinum tubes to hydrogen is naturally due to the formation of similar compounds, but palladium is the most permeable.

[9a] **Rhodium** is generally separated, together with iridium, from the residues left after the treatment of native platinum (note 9), because the palladium is entirely separated from them, and the ruthenium is present in them in very small traces, whilst the osmium at any rate is easily separated, as we shall soon see. The mixture of rhodium and iridium which is left undissolved in dilute aqua regia is dissolved in chlorine water, or by the action of chlorine on a mixture of the metals with sodium chloride. In either case both metals pass into solution. They may be separated by many methods. The rhodium is obtained (if the action be aided by heat) in the form of the chloride $RhCl_3$, and the iridium as iridious chloride, $IrCl_3$. With sodium chloride they both form double salts, which are soluble in water, but the iridium salt is also partially soluble in alcohol, whilst the rhodium salt is not. A mixture of the chlorides, when treated with dilute aqua regia, gives iridic chloride, $IrCl_4$, whilst the rhodium chloride, $RhCl_3$, remains unaltered; ammonium chloride then precipitates the iridium as ammonium iridiochloride, $Ir(NH_4)_2Cl_6$, and on evaporating the rose-coloured filtrate the rhodium gives a crystalline salt, $Rh(NH_4)_3Cl_6$. Rhodium and its various oxides are dissolved when fused with potassium hydrogen sulphate, and give a soluble double sulphate (whilst iridium remains unacted on); this fact is very characteristic for this metal, which offers in its properties many points of resemblance with the iron metals. When fused with potassium hydroxide and chlorate it is oxidised like iridium, but it is not afterwards soluble in water, in which respect it differs from ruthenium. This is taken advantage of for separating rhodium, ruthenium, and iridium. In any case, rhodium under ordinary conditions always gives salts of the type RX_3, and not of any other type; and not only halogen salts, but also oxygen salts, are known in this type, which is rare among the platinum metals. Rhodium chloride, $RhCl_3$, is known in an insoluble anhydrous, and also in a soluble, form (like CrX_3 or salts of chromic oxides), in which it easily gives double salts, compounds with water of crystallisation, and forms rose-coloured solutions. In this form rhodium readily gives double salts of the two types RhM_3Cl_6 and RhM_2Cl_5

alkalies, which form bleaching salts). Among the platinum metals, ruthenium and osmium have the most acid character, and although they give $RuCl_4$ and $OsCl_4$ they are easily oxidised to RuO_4 and OsO_4 by the action of chlorine in the presence of water; the latter are volatile, and may be distilled with the water and hydrochloric acid, from a solution containing other platinum metals.[9b] Thus with respect to

---

—for example, $K_3RhCl_6,3H_2O$ and K_2RhCl_5,H_2O. Solutions of the salts (at least, the ammonium salt) of the first kind give salts of the second kind when they are boiled. If a strong solution of potash is added to a red solution of rhodium chloride and boiled, a black precipitate of the hydroxide $Rh(OH)_3$ is formed; but if the solution of potash is added little by little, it gives a yellow precipitate containing more water. When dissolved in acids, this yellow hydrate of rhodium oxide gives a yellow solution, which only becomes rose-coloured after being boiled. It is obvious that a change takes place here, similar to the transmutations of the salts of chromic oxide. It is also a remarkable fact that the black hydroxide, like many other oxidised compounds of the platinoid metals, does not dissolve in the ordinary oxygen acids, whilst the yellow hydroxide is easily soluble and gives yellow solutions, which deposit imperfectly crystallised salts. Metallic rhodium is easily obtained by igniting its oxygen and other compounds in hydrogen, or by precipitation with zinc. It resembles platinum, and has a sp. gr. of 12·1. At the ordinary temperature it decomposes formic acid into hydrogen and carbonic anhydride (Deville). With the alkali sulphites, the salts of rhodium and iridium of the type RX_3 give sparingly soluble precipitates of double salts of the composition $R(SO_3Na)_3,H_2O$, by means of which these metals may be separated from solution, and also from each other, for a mixture of these salts, when treated with strong sulphuric acid, gives a soluble iridium sulphate and leaves a red insoluble double salt of rhodium and sodium. It may be remarked that the oxides Ir_2O_3 and Rh_2O_3 are comparatively stable and are easily formed, and that they also form different double salts and compounds like the cobaltic compounds (for instance, luteo-salts, $RHX_3,6NH_3$, roseo-salts, $RHX_3H_2O5NH_3$, and purpureo-salts, $IrX_3,5NH_3$, &c.). **Iridious oxide**, Ir_2O_3, is obtained by fusing iridious chloride and its compounds with sodium carbonate and treating the mass with water. The oxide is then left as a black powder, which, when strongly heated, is decomposed into iridium and oxygen; it is easily reduced, and is insoluble in acids, which indicates the feeble basic character of this oxide, in many respects resembling such oxides as cobaltic oxide, ceric or lead dioxide, &c. It does not dissolve when fused with potassium hydrogen sulphate. Rhodium oxide, RH_2O_3, is a far more energetic base. It dissolves when fused with potassium hydrogen sulphate.

From what has been said respecting the separation of platinum and rhodium it will be understood how the compounds of **iridium**, which is the main associate of platinum, are obtained. In describing the treatment of osmiridium we shall again have an opportunity of learning the method of extraction of the compounds of this metal, which has found a technical application in the form of its oxide, Ir_2O_3; this is obtained from many of the compounds of iridium by ignition with water, is easily reduced by hydrogen, and is insoluble in acids. It is used in painting on china, for giving a black colour. Iridium itself is more difficultly fusible than platinum, and when fused does not decompose acids or even aqua regia; it is extremely hard, and is not malleable; its sp. gr. is 22·4. In the form of powder it dissolves in aqua regia, and is even partially oxidised when heated in air, sets fire to hydrogen, and, in a word, closely resembles platinum. Heated in an excess of chlorine it gives iridic chloride, $IrCl_4$, but this loses chlorine at 50°; it is, however, more stable in the form of double salts, which have a characteristic *black* colour—for instance, $Ir(NH_4)_2Cl_6$—but they give iridious chloride, $IrCl_3$, when treated with sulphuric acid.

[9b] We have yet to become acquainted with the two remaining associates of platinum —ruthenium and osmium—whose most important property is that they are oxidised

the types of combination, all the platinum metals, under certain circumstances, give compounds of the type RX_4—for instance, RO_2, RCl_4, &c.

even when heated in air, and that they are able to give **volatile** oxides of the form RuO_4 and OsO_4; these have a powerful odour (like iodine and nitrous anhydride). Both these higher oxides are solids, the former being yellow and the latter white; they volatilise with great ease at 100°. They are known as **ruthenic** and **osmic anhydrides**, although their aqueous solutions (they both slowly dissolve in water) do not show an acid reaction, and although they do not even expel carbonic anhydride from potassium carbonate, do not give crystalline salts with bases, and their alkaline solutions partially deposit them again when boiled (an excess of water decomposes the salts). The formulæ OsO_4 and RuO_4 correspond with the vapour densities of these oxides. Thus Deville found the vapour density of osmic anhydride to be 128 (by the formula 127·5) referred to hydrogen. Tennant and Vauquelin discovered this compound, and Berzelius, Wöhler, Fritzsche, Struve, Deville, Claus, Joly, and others helped in its investigation; nevertheless there are still many questions concerning it which remain unsolved. It should be observed that RO_4 is the highest known form for an oxygen compound, and RH_4 the highest known form for a compound of hydrogen; whilst the highest forms of acid hydrates are SiH_4O_4, PH_3O_4, SH_2O_4, $ClHO_4$—all with four atoms of oxygen, and therefore in this number there is apparently the limit for the simple forms of combination of hydrogen and oxygen. In combination with *several* atoms of an element, or several elements, there may be more than O_4 or H_4, but a molecule never contains more than four atoms of either O or H to one atom of another element. Thus the simplest forms of combination of hydrogen and oxygen are exhausted by the list RH_4, RH_3, RH_2, RH, RO, RO_2, RO_3, RO_4. The extreme members are RH_4 and RO_4, and are only met with for such elements as carbon, silicon, osmium, ruthenium, which also give RCl_4 with chlorine. In these extreme forms, RH_4 and RO_4, the compounds are the least stable (compare SiH_4, PH_3, SH_2, ClH, or RuO_4, MoO_3, ZrO_2, SrO), and easily give up part, or even the whole, of their oxygen or hydrogen.

The primary source from which the compounds of ruthenium and osmium are obtained is either **osmiridium** (the osmium predominates, from IrOs to $IrOs_4$, sp. gr. from 16 to 21), which occurs in platinum ores (it is distinguished from the grains of platinum by its crystalline structure, hardness, and insolubility in aqua regia), or else those insoluble residues which are obtained, as we saw above, after treating platinum with aqua regia. Osmium predominates in these materials, which sometimes contain from 30 to 40 per cent. of it, and rarely more than 4 to 5 per cent. of ruthenium. The process for their treatment is as follows: they are first fused with 6 parts of zinc, and the zinc is then extracted with dilute hydrochloric acid. The osmiridium thus treated is, according to Fritzsche and Struve's method, then added to a fused mixture of potassium hydroxide and chlorate in an iron crucible; the mass, as it begins to evolve oxygen, acts on the metal, and the reaction afterwards proceeds spontaneously. The dark product is treated with water, and gives a solution of osmium and ruthenium in the form of soluble salts, R_2OsO_4 and R_2RuO_4, whilst the insoluble residue contains a mixture of oxides of iridium (and some osmium, rhodium, and ruthenium), and grains of metallic iridium still unacted on. According to Frémy's method, the lumps of osmiridium are straightway heated to whiteness in a porcelain tube in a stream of air or oxygen, when the very volatile osmic anhydride is obtained directly, and is collected in a well-cooled receiver, whilst the ruthenium gives a crystalline sublimate of the dioxide, RuO_2, which is, however, very difficultly volatile (it volatilises together with osmic anhydride), and therefore remains in the cooler portions of the tube; this method does not give volatile ruthenic anhydride, and the iridium and other metals are not oxidised or give non-volatile products. This method is simple, and at once gives pure dry osmic anhydride in the receiver, and ruthenium dioxide in the sublimate. The air which passes through the tube should be previously passed through sulphuric acid, not only in order to dry it, but also to remove the organic and reducing dust. The vapour of osmic anhydride must be powerfully cooled, and ultimately passed over caustic potash. A

But this is the highest form only for platinum and palladium. Further, the remaining platinum metals, **like iron, give acids** of the type

---

third mode of treatment, which is most frequently employed, was proposed by Wöhler, and consists in slightly heating (in order that the sodium chloride should not melt) an intimate mixture of osmiridium and common salt in a stream of moist chlorine. The metals then form compounds with chlorine and sodium chloride, whilst the osmium forms the chloride, $OsCl_4$, which reacts with the moisture, and gives osmic anhydride, which is condensed. The ruthenium in this, as in the other processes, does not directly give ruthenic anhydride, but is always extracted as the soluble ruthenium salt, K_2RuO_4, obtained by fusion with potassium hydroxide and chlorate or nitrate. When the orange-coloured ruthenate, K_2RuO_4, is mixed with acids, the liberated ruthenic acid immediately decomposes into the volatile ruthenic anhydride and the insoluble ruthenic oxide: $2K_2RuO_4 + 4HNO_3 = RuO_4 + RuO_2,2H_2O + 4KNO_3$. When once one of the above compounds of ruthenium or osmium is procured, it is easy to obtain all the remaining compounds, and by reduction (by metals, hydrogen, formic acid, &c.) the metals themselves.

Osmic anhydride, OsO_4, is very easily deoxidised by many methods. It blackens organic substances, owing to reduction, and is therefore used in investigating vegetable and animal, and especially nerve, preparations under the microscope. Although osmic anhydride may be distilled in hydrogen, yet complete reduction is accomplished when a mixture of hydrogen and osmic anhydride is slightly ignited (just before it inflames). If osmium be placed in the flame it is oxidised, and gives vapours of osmic anhydride, which become reduced, and the flame gives a brilliant light. Osmic anhydride deflagrates like nitre on red-hot charcoal; zinc, and even mercury and silver, reduce osmic anhydride from its aqueous solutions into the lower oxides or metal; such reducing agents as hydrogen sulphide, ferrous sulphate or sulphurous anhydride, alcohol, &c., act in the same manner with great ease.

The lower oxides of osmium, ruthenium, and of the other elements of the platinum series are not volatile, and it is noteworthy that the other elements behave differently. On comparing SO_2, SO_3; As_2O_3, As_2O_5; P_2O_3, P_2O_5; CO, CO_2, &c., we observe a converse phenomenon; the higher oxides are less volatile than the lower. In the case of osmium all the oxides, with the exception of the highest, are non-volatile, and it may therefore be thought that this higher form is more highly constituted than the lower. It is possible that osmic oxide, OsO_2, stands in the same relation to the anhydride as C_2H_4 to CH_4—i.e., the lower oxide is perhaps Os_2O_4, or is still more polymerised, which would explain why the lower oxides, having a greater molecular weight, are less volatile than the higher oxides, just as we saw in the case of the nitrogen oxides, N_2O and NO.

Ruthenium and **osmium**, obtained by the ignition or reduction of their compounds in the form of powder, have a density considerably less than in the fused form, and differ in this condition in their capacity for reaction; they are much more difficultly fused than platinum and iridium, although ruthenium is more fusible than osmium. *Ruthenium* in powder has a specific gravity of 8·5, the fused metal of 12·2; *osmium* in powder has a specific gravity of 20·0, and when semi-fused—or, more strictly speaking, agglomerated—in the oxyhydrogen flame, of 21·4, and when fused 22·5. The powder of slightly heated osmium oxidises very easily in the air, and when ignited burns like tinder, forming directly the odoriferous and highly poisonous osmic anhydride (hence its name, from the Greek word ὀσμή, or ὀσμός, odour); ruthenium also oxidises when heated in air, but with more difficulty, forming the oxide, RuO_2. The oxides of the types RO, R_2O_3, and RO_2 (and their hydrates) obtained by reduction from the higher oxides, and also from the chlorides, are analogous to those given by the other platinum metals, in which respect osmium and ruthenium closely resemble them. We may also remark that ruthenium has been found in the platinum deposits of Borneo in the form of *laurite*, Ru_2S_3, in grey octahedra of sp. gr. 7·0.

For osmium, Moraht and Wischin (1893) obtained free osmic acid, H_2OsO_4, by

RO_3 or hydrates, $H_2RO_4=RO_2(HO)_2$ (the type of sulphuric acid); but these, like ferric and manganic acids, are chiefly known in the form of salts of the composition K_2RO_4 or $K_2R_2O_7$ (like the dichromate). These salts are obtained, like the manganates and ferrates, by fusing the oxides, or even the metals themselves, with nitric, or, better still, potassium peroxide. They are soluble in water, are easily deoxidised and do not yield the acid anhydrides under the action of acids, but break up, either (like the ferrate) forming oxygen and a basic oxide (iridium and rhodium react in this manner, as they do not give higher forms of oxidation), or passing into a lower and higher form of oxidation—that is, reacting like a manganate (or partly like a nitrite or phosphite). Osmium and ruthenium react according to the latter form, as they are capable of giving **higher forms of oxidation**, OsO_4 and RuO_4, and therefore their reactions of decomposition may be essentially represented by the equation: $2OsO_3=OsO_2+OsO_4$.[10]

---

decomposing K_2OsO_4 with water, and precipitating with alcohol in a current of hydrogen (because in air volatile OsO_4 is formed); with H_2S osmic acid gives $OsO_3(HS)_2$ at the ordinary temperature.

Debray and Joly showed that ruthenic anhydride, RuO_4, fuses at 25°, boils at 100°, and evolves oxygen when dissolved in potash, forming the salt $KRuO_4$ (not isomorphous with potassium permanganate).

Joly (1891), who studied the ruthenium compounds in greater detail, showed that the easily formed $KRuO_4$ gives $RuKO_4,RuO_3$ when ignited, but it resembles $KMnO_4$ in many respects. In general, Ru has much in common with Mn. Joly (1889) also showed that if KNO_3 is added to a solution of $RuCl_3$ containing HCl, the solution becomes hot, and a salt, $RuCl_3NO,2KCl$, is formed, which enters into double decomposition and is very stable. Moreover, if $RuCl_3$ be treated with an excess of nitric acid, it forms a salt, $RuCl_3NO,H_2O$, on heating (to boiling) and adding HCl. The vapour density of RuO_4 (Debray and Joly) corresponds to that formula.

[10] Although palladium gives the same types of combination (with chlorine) as platinum, its reduction to RX_2 is incomparably easier than that of platinic chloride, and in the case of iridium it is also very easy. Iridic chloride, $IrCl_4$, acts as an oxidising agent, readily parts with a fourth of its chlorine to a number of substances, readily evolves chlorine when heated, and it is only at low temperatures that chlorine and aqua regia convert iridium into iridic chloride. In disengaging chlorine, iridium more often and easily gives the very stable iridious chloride, $IrCl_3$ (this substance is perhaps $Ir_2Cl_6=IrCl_2,IrCl_4$)—which is insoluble in water, but soluble in potassium chloride (because it forms the double salt K_3IrCl_6)—than the dichloride, $IrCl_2$. This compound, corresponding with IrX_2, is very stable, and corresponds with the **basic oxide**, Ir_2O_3, resembling the oxides Fe_2O_3, Co_2O_3. To this form there correspond ammoniacal compounds similar to those given by cobaltic oxide. Although iridium also gives an acid in the form of the salt $K_2Ir_2O_7$, it does not, like iron (and chromium), form the corresponding chloride, $IrCl_6$. In general, in this as in the other elements, it is impossible to predict the chlorine compounds from those of oxygen. In this respect rhodium is very much like iridium (as platinum is like palladium). For $RhCl_4$ decomposes with extreme ease, whilst rhodium chloride, $RhCl_3$, is very stable, like many of the salts of the type RhX_3. There is as close a resemblance between osmium and ruthenium. As a rule this acid character is more developed in osmium than in platinum and iridium. In general, the platinum metals subject themselves to the periodic law with perfect clearness, and their investigation is greatly facilitated by this means.

Platinum and its analogues, like iron and its analogues, are able to form complex and comparatively stable cyanogen and ammonia compounds, corresponding with the ferrocyanides and the ammoniacal compounds of cobalt, which we have already considered in the preceding chapter.

If platinous chloride, $PtCl_2$ (insoluble in water), is added by degrees to a solution of potassium cyanide, it is completely dissolved (like silver chloride), and, on evaporating, the solution deposits rhombic prisms of **potassium platinocyanide**, $PtK_2(CN)_4,3H_2O$. This salt, like all those corresponding with it, has a remarkable play of colours, due to the phenomena of dichroism, and even polychroism, natural to all the platinocyanides. Thus it is yellow and reflects a bright-blue light. It is easily soluble in water, effloresces in air, then turns red, and at 100° orange, when it loses all its water. The loss of water does not destroy its stability—that is, it still remains unchanged, and its stability is further shown by the fact that it is formed when potassium ferrocyanide, $K_4Fe(CN)_6$, is heated with platinum black. This salt, first obtained by Gmelin, shows a neutral reaction with litmus; it is exceedingly stable under the action of air, like potassium ferrocyanide, which it resembles in many respects. Thus the platinum in it cannot be detected by reagents such as sulphuretted hydrogen,[10a] the potassium may be replaced by other metals by the action of their salts, so that it corresponds with a whole series of compounds, $R_2Pt(CN)_4$, and it is stable, although the potassium cyanide and platinous salts, of which it is composed, individually easily undergo change. When treated with oxidising agents it passes, like the ferrocyanide, into a higher form of combination of platinum. If salts of silver be added to its solution, it gives a heavy white precipitate of silver platinocyanide, $PtAg_2(CN)_4$, which, when treated with sulphuretted hydrogen, forms insoluble Ag_2S, and soluble **hydroplatinocyanic acid**, $H_2Pt(CN)_4$. If potassium platinocyanide be mixed with an equivalent quantity of sulphuric acid, the hydroplatinocyanic acid liberated may be extracted by a mixture of alcohol and ether, which does not dissolve the K_2SO_4 formed. The ethereal solution, when evaporated in a desiccator, deposits bright-red crystals of the composition $PtH_2(CN)_4,5H_2O$. This acid colours litmus paper, liberates carbonic anhydride from sodium carbonate, and saturates alkalies, so that it presents an analogy to hydroferrocyanic acid.[11]

[10a] It may also, therefore, be classed among the 'complex' compounds.

[11] This acid character is explained by the influence of the platinum on the hydrogen, and by the attachment of the cyanogen groups. Thus, cyanuric acid, $H_3(CN)_3O_3$, is an energetic acid compared with cyanic acid, HCNO. And the formation of a compound with five molecules of water of crystallisation, $[PtH_2(CN)_4,5H_2O]$, confirms the opinion

Ammonia, like potassium cyanide, has the faculty of easily reacting with platinum dichloride, forming compounds which are similar to those

---

that platinum is able to form compounds of still higher types than that expressed in its saline compounds.

A whole series of **platinocyanides** of the common type $PtR_2(CN)_4,nH_2O$ is obtained by means of double decomposition with the potassium or hydrogen or silver salts. For example, the salts of sodium and lithium contain, like the potassium salt, three molecules of water. The sodium salt is soluble in water and alcohol. The ammonium salt has the composition $Pt(NH_4)_2(CN)_4,2H_2O$ and gives crystals which reflect blue and rose-coloured light. This ammonium salt decomposes at 300°, with evolution of water and ammonium cyanide, leaving a greenish **platinum dicyanide**, $Pt(CN)_2$, which is insoluble in water and acid, but dissolves in potassium cyanide, hydrocyanic acid, and other cyanides. The same platinous cyanide is obtained by the action of sulphuric acid on the potassium salts in the form of a reddish-brown amorphous precipitate. The most characteristic of the platinocyanides are those of the alkaline earths. The magnesium salt, $PtMg(CN)_4,7H_2O$, crystallises in regular prisms, the side faces of which are of a metallic-green colour and the terminal planes dark blue. It shows a carmine-red colour along the main axis, and dark red along the lateral axis; it easily loses water, $(2H_2O)$, at 40° and then turns blue (it then contains $5H_2O$, which is frequently the case with the platinocyanides). Its aqueous solution is colourless, and an alcoholic solution deposits yellow crystals. The remainder of the water is given off at 230°. It is obtained by saturating platinocyanic acid with magnesia, or else by double decomposition between the barium salt and magnesium sulphate. The strontium salt, $SrPt(CN)_4,4H_2O$, crystallises in milk-white plates having a violet and green iridescence. When it effloresces in a desiccator, its surfaces have a violet and metallic-green iridescence. A colourless solution of the barium salt, $PtBa(CN)_4,4H_2O$, is obtained by saturating a solution of hydroplatinocyanic acid with baryta, or by boiling the insoluble copper platinocyanide in baryta water. It crystallises in monoclinic prisms of a yellow colour, with blue and green iridescence; it loses half its water at 100°, and the whole at 150°. The ethyl salt, $Pt(C_2H_5)_2(CN)_4,2H_2O$, is also very characteristic; its crystals are isomorphous with those of the potassium salt, and are obtained by passing hydrochloric acid into an alcoholic solution of hydroplatinocyanic acid. The facility with which they crystallise, the regularity of their forms, and their remarkable play of colours render the preparation of the platinocyanides one of the most attractive lessons of the laboratory. The barium salt is often employed in experiments with the Röntgen rays in investigating the radio-active substances, as it becomes very phosphorescent under the influence of these rays.

By the action of chlorine or dilute nitric acid the platinocyanides are converted into salts of the composition $PtM_2(CN)_5$, which corresponds with $Pt(CN)_3,2KCN$—that is, they express the type of a non-existent form of oxidation of platinum, PtX_3 (i.e., of the oxide Pt_2O_3), just as potassium ferricyanide, $(FeCy_3,3KCy)$, corresponds with ferric oxide, and the ferrocyanide with ferrous oxide. The potassium salt of this series, $PtK_2(CN)_5,3H_2O$, forms regular brown prisms with a metallic lustre, and is soluble in water but insoluble in alcohol. Alkalies re-convert this compound into the ordinary platinocyanide, $K_2Pt(CN)_4$, taking up the excess of cyanogen. It is remarkable that the salts of the type PtM_2Cy_5 contain the same amount of water of crystallisation as those of the type PtM_2Cy_4. Thus, the salts of potassium and lithium contain three, and the salt of magnesium seven, molecules of water, like the corresponding salts of the type of platinous oxide. Moreover, neither platinum nor any of its associates gives any cyanogen compound corresponding with the oxide, i.e., having the composition PtK_2Cy_6, just as there are no compounds higher than those which correspond to $RCy_3,nMCy$ for cobalt or iron. This would appear to indicate the absence of any such double complex cyanides. The phenomenon is perhaps connected with the faculty of cyanogen of giving tricyanogen polymerides, such as cyanuric acid, solid cyanogen chloride, &c. Under the action of an excess of chlorine, a solution of $PtK_2(CN)_4$ gives (besides PtK_2Cy_5) a product, $PtK_2Cy_4Cl_2$, which given by cobalt and are comparatively stable. But as ammonia does not contain any hydrogen easily replaceable by metals, and as ammonia

---

evidently contains the form PtX_4, but at first the action of the chlorine (or the electrolysis of, or addition of dilute peroxide of hydrogen to, a solution of PtK_2Cy_4, acidulated with hydrochloric acid) produces an easily soluble intermediate salt which crystallises in thin copper-red needles (Wilm, 1889, and others). It apparently corresponds to a compound $5PtK_2Cy_4 + PtK_2Cy_4Cl_2 + 24H_2O$. Under the action of an excess of ammonia, both these chlorine products are converted either completely or in part (according to Wilm, ammonia does not act upon PtK_2Cy_4) into $PtCy_2,2NH_3$, i.e., a platino-ammonia compound (see further on). It is also necessary to pay attention to the fact that ruthenium and osmium —which, as we know, give higher forms of oxidation than platinum—are also able to combine with a larger proportion of potassium cyanide (but not of cyanogen) than platinum. Ruthenium forms a crystalline **hydroruthenocyanic acid,** $RuH_4(CN)_6$, which is soluble in water and alcohol, and corresponds with the salts $M_4Ru(CN)_6$. There are exactly similar osmic compounds—for example, $K_4Os(CN)_6,3H_2O$. The latter is obtained in the form of colourless, sparingly soluble regular tablets on evaporating the solution obtained from a fused mixture of potassium osmiochloride, K_2OsCl_6, and potassium cyanide. These osmic and ruthenic compounds fully correspond with potassium ferrocyanide, $K_4Fe(CN)_6,3H_2O$, not only in their composition, but also in their crystalline form and reactions, again demonstrating the close analogy between iron, ruthenium, and osmium, which we have shown by giving these three elements a similar position (in the eighth group in the periodic system). For rhodium and iridium only salts of the same type as the ferricyanides, M_3RCy_6, are known, and for palladium only those of the type M_2PdCy_4, which are analogous to the platinum salts. In all these examples a **constancy of the types** of the double cyanides is apparent. In the eighth group we have iron, cobalt, nickel, copper, and their analogues, ruthenium, rhodium, palladium, silver, and also osmium, iridium, platinum, gold. The double cyanides of iron, ruthenium, and osmium have the type $K_4R(CN)_6$; those of cobalt, rhodium, and iridium, the type $K_3R(CN)_6$; of nickel, palladium, and platinum, the types $K_2R(CN)_4$ and $K_2R(CN)_5$; and for copper, silver, and gold there are known $KR(CN)_2$, so that the presence of 4, 3, 2, and 1 atoms of potassium corresponds with the order of the elements in the periodic system. Those types which we have seen in the ferrocyanides and ferricyanides of iron repeat themselves in all the platinum metals, and this naturally leads to the conclusion that the formation of similar so-called double complex salts is of exactly the same nature as that of the ordinary salts. If, in expressing the union of the elements in the oxygen acids, the existence of an aqueous residue (hydroxyl group) be admitted, in which the hydrogen is replaced by a metal, we have then only to apply this mode of expression to the double salts, and the analogy will be obvious, if only we remember that Cl_2, C_2N_2, SO_4, &c., are equivalent to O. So that wherever OH can stand there also can $Cl_2H,(CN)_2H$, SO_4H, &c., stand. They all $= X$, and therefore, in point of fact, wherever X ($= Cl$ or OH, &c.) can be placed, (Cl_2H), (SO_4H), &c., can also stand. And as $Cl_2H = Cl + HCl$ and $SO_4H = OH + SO_3$, &c., it follows that molecules HCl or SO_3, or, in general, whole molecules—for instance, NH_3, H_2O, salts, &c.—can annex themselves to a compound containing X. This is an indirect consequence of the law of substitution, which explains the origin of double salts, ammonia compounds, compounds with water of crystallisation, &c., by one general method. Thus, the double salt $MgSO_4,K_2SO_4$, according to this reasoning, *may be* considered as a substance of the same type as $MgCl_2$, namely, as $= Mg(SO_4K)_2$, and the alums as derived from $Al(OH)(SO_4)$, namely, as $Al(SO_4K)(SO_4)$. Without stopping to pursue this digression further, we shall apply these considerations to the type of the ferrocyanides and ferricyanides and their platinum analogues. Such a salt as K_2PtCy_4 may accordingly be regarded as $Pt(Cy_2K)_2$, like $Pt(OH)_2$; and such a salt as PtK_2Cy_5 as $PtCy(Cy_2K)_2$, the analogue of $PtX(OH)_2$, or $AlX(OH)_2$, and other compounds of the type RX_3. Potassium ferricyanide and the analogous compounds of cobalt, iridium, and rhodium belong to the same type, with the same difference as there is between $RX(OH)_2$ and $R(OH)_3$, since $FeK_3Cy_6 = Fe(Cy_2K)_3$. Limiting myself to these considerations, itself is able to combine with acids, the PtX_2 plays, as it were, the part of an acid with reference to the ammonia. Owing to the influence of

which may partially elucidate the nature of double salts, I shall now pass again to the complex saline compounds known for platinum.

(*A*) **Platinous chloride,** $PtCl_2$, which is insoluble in water, forms **double salts with the metallic chlorides.** These double chlorides are soluble in water, and capable of crystallising. Hence, when a hydrochloric acid solution of platinous chloride is mixed with solutions of metallic salts and evaporated, it forms crystalline salts of a red or yellow colour. Thus, for example, the potassium salt, PtK_2Cl_4, is red, and easily soluble in water; the sodium salt is soluble also in alcohol; the barium salt, $PtBaCl_4,3H_2O$, is soluble in water, but the silver salt, $PtAg_2Cl_4$, is insoluble and may be used for obtaining the remaining salts by means of double decomposition with their chlorides.

(*B*) On mixing solutions of potassium thiocyanate and potassium platinochloride, K_2PtCl_4, they form a double thiocyanate, $PtK_2(CNS)_4$, which is easily soluble in water and alcohol, crystallises in red prisms, and gives an orange-coloured solution, which precipitates salts of the heavy metals. The action of sulphuric acid on the lead salt of the same type gives the acid itself, $PtH_2(SCN)_4$, which corresponds with these salts. The type of these compounds is evidently the same as that of the cyanides.

(*C*) A remarkable example of the complex compounds of platinum was observed by Schützenberger (1868). He showed that finely divided platinum in the presence of chlorine and carbonic oxide at 250°–300° gives phosgene and a volatile compound containing platinum. The same substance is formed by the action of carbonic oxide on platinous chloride. It decomposes with an explosion in contact with water. Carbon tetrachloride dissolves a portion of this substance, and on evaporation gives crystals of $2PtCl_2,3CO$, whilst the compound $PtCl_2,2CO$ remains undissolved. When fused and sublimed it gives yellow needles of $PtCl_2,CO$, and in the presence of an excess of carbonic oxide $PtCl_2,2CO$ is formed. These compounds are fusible (the first at 250°, the second at 142°, and the third at 195°). In this case (as in the double cyanides) combination takes place, because both carbonic oxide and platinous chloride are unsaturated compounds capable of further combination. The carbon tetrachloride solution absorbs NH_3 and gives $PtCl_2,CO,2NH_3$, and $PtCl_2,2CO,2NH_3$, and these substances are analogous (Foerster, Zeisel, Jörgensen) to similar compounds containing complex amines (for instance, pyridine, C_5H_5N), instead of NH_3, and ethylene, &c., instead of CO, so that here we have a whole series of complex platino-compounds. The compound $PtCl_2,CO$ dissolves in hydrochloric acid without change, and the solution disengages all the carbonic oxide when KCN is added to it, which shows that those forces which bind 2 molecules of KCN to $PtCl_2$ can also bind the molecule CO, or 2 molecules of CO. When the hydrochloric acid solution of $PtCl_2,CO$ is mixed with a solution of sodium acetate or acetic acid, it gives a precipitate of PtOCO, i.e., the Cl_2 is replaced by oxygen (probably because the acetate is decomposed by water). This oxide, PtOCO, splits up into $Pt+CO_2$ at 350°. PtSCO is obtained by the action of sulphuretted hydrogen upon $PtCl_2CO$. All this leads to the conclusion that the group PtCO is able to assimilate $X_2=Cl_2$, S, O, &c. (Mylius, Foerster, 1891). Pullinger (1891), by igniting spongy platinum at 250°, first in a stream of chlorine and then in a stream of carbonic oxide, obtained (besides volatile products) a non-volatile yellow substance which remained unchanged in air and disengaged chlorine and phosgene gas when ignited; its composition was $PtCl_6(CO)_2$, which apparently proves it to be a compound of $PtCl_2$ and $2COCl_2$, as $PtCl_2$ is able to combine with oxychlorides, and forms somewhat stable compounds.

(*D*) The faculty of platinous chloride for forming stable compounds with divers substances shows itself in the formation of the compound $PtCl_2,PCl_3$ by the action of phosphorus pentachloride at 250° on platinum powder (Pd reacts in a similar manner, according to Fink, 1892). The product contains both phosphorus pentachloride and platinum, whilst the presence of $PtCl_2$ is shown in the fact that the action of water produces **chlorplatino-phosphorous acid,** $PtCl_2P(OH)_3$.

the ammonia, the X_2 in the resultant compound will represent the same character as it has in ammoniacal salts ; consequently the ammoniacal

(*E*) After the cyanides, the **double salts** of platinum **formed by sulphurous acid** are most distinguished for their stability and characteristic properties. This is all the more instructive, as sulphurous acid is only feebly energetic, and, moreover, in these, as in all its compounds, it exhibits a dual reaction. The salts of sulphurous acid, R_2SO_3, either react as salts of a feeble dibasic acid, where the group SO_3 presents itself as bivalent, and consequently equal to X_2, or else they react after the manner of salts of a monobasic acid containing the same residue, RSO_3, as occurs in the salts of sulphuric acid. In sulphurous acid this residue is combined with hydrogen, $H(SO_3H)$, whilst in sulphuric acid it is united with the aqueous residue (hydroxyl), $OH(SO_3H)$. These two forms of action of the sulphites appear in their reactions with the platinum salts—that is to say, salts of both kinds are formed, and they both correspond with the type PtH_2X_4. The one series of salts contain $PtH_2(SO_3)_2$, and their reactions are due to the bivalent residue of sulphurous acid, which replaces X_2. The others, which have the composition $PtR_2(SO_3H)_4$, contain sulphoxyl. The latter salts will evidently react like acids; they are formed simultaneously with the salts of the first kind, and pass into them. These salts are obtained either by directly dissolving platinous oxide in water containing sulphurous acid, or by passing sulphurous anhydride into a solution of platinous chloride in hydrochloric acid. If a solution of platinous chloride or platinous oxide in sulphurous acid be saturated with sodium carbonate, it forms a white, sparingly soluble precipitate containing $PtNa_2(SO_3Na)_4,7H_2O$. If this precipitate is dissolved in a small quantity of hydrochloric acid and left to evaporate at the ordinary temperature, it deposits a salt of the other type, $PtNa_2(SO_3)_2,H_2O$, in the form of a yellow powder, which is sparingly soluble in water. The potassium salt analogous to the first salt, $PtK_2(SO_3K)_4,2H_2O$, is precipitated by passing sulphurous anhydride into a solution of potassium sulphite in which platinous oxide is suspended. A similar salt is known for ammonium, and with hydrochloric acid it gives a salt of the second kind, $Pt(NH_4)_2(SO_3)_2,H_2O$. If ammonio-chloride of platinum is added to an aqueous solution of sulphurous anhydride, it is first deoxidised and chlorine is evolved, forming a salt of the type PtX_2; a double decomposition then takes place with the ammonium sulphite, and a salt of the composition $Pt(NH_4)_2Cl_3(SO_3H)$ is formed (in a desiccator). The acid character of this substance is explained by the fact that it contains the elements SO_3H—sulphoxyl, with the hydrogen not yet displaced by a metal. On saturating a solution of this acid with potassium carbonate it gives orange-coloured crystals of a potassium salt of the composition $Pt(NH_4)_2Cl_2(SO_3K)$. Here it is evident that an equivalent of chlorine in $Pt(NH_1)_2Cl$ is replaced by the univalent residue of sulphurous acid. Among these salts, that of the composition $Pt(NH_4)_2Cl_2(SO_3H)_2,H_2O$ is very readily formed, and crystallises in well-formed colourless crystals; it is obtained by dissolving ammonium platinochloride, $Pt(NH_4)_2Cl_4$, in an aqueous solution of sulphurous acid. The difficulty with which sulphurous anhydride and platinum are separated from these salts indicates the same basic character in these compounds as is seen in the double cyanides of platinum. In their passage into a complex salt, the metal platinum and the group SO_2 modify their relations (compared with those of PtX_2 or SO_2X_2), just as the chlorine in the salts $KClO$, $KClO_3$, and $KClO_4$ is modified in its relations as compared with that in hydrochloric acid or potassium chloride.

(*F*) No less characteristic are the double **platinonitrites** (Co gives similar compounds). They correspond with nitrous acid, whose salts, RNO_2, contain the univalent radicle, NO_2, which is capable of replacing chlorine, so that the salts of this kind should form a common type, $PtR_2(NO_2)_4$, and such a salt of potassium has actually been obtained by mixing a solution of potassium platinochloride with a solution of potassium nitrite, when the liquid becomes colourless, especially if heated, indicating the change in the chemical distribution of the elements. As the liquid decolorises it gradually deposits sparingly soluble colourless prisms of the potassium salt, $K_2Pt(NO_2)_4$, which does not contain any water. With silver nitrate a solution of this salt gives a precipitate compounds produced from PtX_2 will be salts in which X will be replaceable by various other haloids. **The platino-ammonium compounds** form compounds of PtX_2 with $2NH_3$, and with $4NH_3$. PtX_4 gives (not directly from PtX_4 and ammonia, but from the compounds of PtX_2 by the action of chlorine, &c.) similar compounds with $2NH_3$ and with $4NH_3$.[12]

of silver platinonitrite, $PtAg_2(NO_2)_4$. The silver of this salt may be replaced by other metals by means of double decomposition with metallic chlorides. The sparingly soluble barium salt, when treated with an equivalent quantity of sulphuric acid, gives a soluble acid, which separates, under the receiver of an air-pump, in red crystals; this acid has the composition $PtH_2(NO_2)_4$. To the potassium salt, $K_2Pt(NO_2)_4$, there correspond (Vizes, 1892) $K_2Pt(NO_2)_4Br_2$ and $K_2Pt(NO_2)_4Cl_2$ and other compounds of the same type, K_2PtX_6, where X is partly replaced by Cl or Br and partly by (NO_2), showing a transition towards the type of the double salts like the platino-ammoniacal salts.

In all the preceding complex compounds of Pt we see a common type, $PtX_2,2MX$ (i.e., of double salts corresponding to PtO) or $PtM_2X_4 = Pt(MX_2)_2$, corresponding to $Pt(HO)_2$, with the replacement of O by its equivalent X_2. The fact of so many of these complex compounds (see notes 12–14) being accumulated around Pt is doubtless no matter of chance. This is already seen in the many points of resemblance exhibited externally by these compounds, and is probably connected with the small energy of the salt-forming power of platinum and with its polyvalency in a state of combination. The elements prone to give such 'complex' compounds, like Cr, Co, Fe, Mo, W, &c., exhibit the same features, and there is reason for supposing that certain peculiarities in the reactions of organic compounds (for instance, the non-saline reactions of the products of metalepsis and the slow rate of many reactions, &c.) depend on the same causes as those which lead to the formation of 'complex' compounds. This subject, I think, presents one of the most important and interesting problems to be solved by the chemistry of the near future, and one which might also throw much light on the vaguely understood provinces of solutions and of the forces governing the formation of chemical compounds.

[12] Considering it unprofitable to discuss the merits of the numerous hypotheses which have been put forward at different times respecting the structure of the platino-ammonia compounds, as none of them brought any new facts to light, and all were limited to a pictorial representation of what was already known, I think it best, as far as possible, to unite the ammonia compounds of platinum with the other explained 'complex' compounds of platinum which have been more or less fully explained in the preceding notes (especially note 11). It seems to me that it is most important *as a commencement* to render clear the analogy in the formation of various complex compounds, and it is this analogy of the ammonia compounds with those containing water of crystallisation and double salts that forms the main object of the primary generalisation. We recognise in platinum, at all events, not only the four affinities expressed in the compound $PtCl_4$, but a much larger number of them, if only the *summation of affinities* is actually possible. Thus, in sulphur we recognise not two, but a much greater number of affinities; it is clear that at least six affinities can act. So also among the analogues of platinum: osmic anhydride, OsO_4, $Ni(CO)_4$, PtH_2Cl_6, &c., indicate the existence of at least eight affinities; whilst, in chlorine, judging from the compound $KClO_4 = ClO_3(OK) = ClX_7$, we must recognise at least seven affinities, instead of the one usually accepted. The latter mode of calculating affinities is a tribute to that period of the development of science when only the simplest hydrogen compounds were considered, and when all complex compounds were entirely neglected (they were placed in the class of molecular compounds). This is insufficient for the present state of knowledge, because we find that, in complex compounds, as in the most simple, the same constant types or modes of equilibrium are repeated, and the character of certain elements is greatly modified in the passage from the most simple into very complex compounds.

Judging from the most complex platino-ammonium compounds, $PtCl_4,4NH_3$, we should admit the possibility of the formation of compounds of the type PtX_4Y_4, where

If ammonia acts on a boiling solution of platinous chloride in hydrochloric acid, it produces the green **salt of Magnus** (1829), $PtCl_2,2NH_3$, insoluble in water and hydrochloric acid. But, judging by its reactions, this salt has twice the above formula. Thus, Gros (1837), on boiling Magnus' salt with nitric acid, observed that half the chlorine was replaced by the residue of nitric acid and half the platinum was disengaged: $2PtCl_2(NH_3)_2+2HNO_3=PtCl_2(NO_3)_2(NH_3)_4+Pt,2HCl$. The **Gros' salt** thus obtained, $PtCl_2(NO_3)_2,4NH_3$ (if Magnus' salt

---

$Y_4=4X_2=4NH_3$, and this shows that those forces which form such a characteristic series of double platinocyanides, $PtK_2(CN)_4,8H_2O$, probably also determine the formation of the higher ammonia derivatives, as is seen on comparing—

$PtCl_2$	NH_3	Cl_2	$8NH_3$
$Pt(CN)_2$	KCN	KCN	$8H_2O$.

Moreover, it is obviously much more natural to ascribe the faculty for combination with nY to the whole of the acting elements—that is, to PtX_2 or PtX_4, and not to platinum alone. Naturally such compounds are not produced with every Y. With certain X's there only combine certain Y's. The best known and most frequently formed compounds of this kind are those with water—that is, compounds with water of crystallisation. Compounds with salts are double salts; also we know that similar compounds are frequently formed by means of ammonia. Salts of zinc, ZnX_2, copper, CuX_2, silver, AgX, and many others give similar compounds; but these and many other **ammonio-metallic** saline compounds are unstable, and readily part with their combined ammonia, and it is only in the elements of the platinum group and in the group of the analogues of iron that we observe the faculty to form stable ammonio-metallic compounds. It must be remembered that the metals of the platinum and iron groups are able to form several high grades of oxidation which have an acid character, and consequently in the lower degrees of combination there yet remain affinities capable of retaining other elements, and they probably retain ammonia, and hold it the more stably, because all the properties of the platinum compounds are rather acid than basic—that is, PtX_n recalls HX or SnX_n or CX_n rather than KX, CaX_2, BaX_2, &c., and ammonia naturally will rather combine with an acid than with a basic substance. Further, a dependence, or certain connection of the forms of oxidation with the ammonia compounds, is seen on comparing the following compounds:—

$PdCl_2,2NH_3,H_2O$	$PdCl_2,4NH_3,H_2O$
$PtCl_2,2NH_3$	$PtCl_4,4NH_3$
$RhCl_3,5NH_3$	$RuCl_2,4NH_3,8H_2O$
$IrCl_3,5NH_3$	$OsCl_2,4NH_3,2H_2O$

We know that platinum and palladium give compounds of lower types than iridium and rhodium, whilst ruthenium and osmium give the highest forms of oxidation; this shows itself in this case also. We have purposely cited the same compounds with $4NH_3$ for osmium and ruthenium as we have for platinum and palladium, and it is then seen that Ru and Os are capable of retaining $2H_2O$ and $8H_2O$, besides Cl_2 and NH_3, which the compounds of platinum and palladium are unable to do. The same ideas which were developed in note 35, Chap. XXII., respecting the cobaltia compounds are perfectly applicable to the present case, i.e., to the **platinia** compounds or ammonia compounds of the platinum metals, among which Rh and Ir give compounds which are completely analogous to the cobaltia compounds.

Iridium and rhodium, which readily give compounds of the type RX_3, give compounds (Claus) of the type $IrX_3,5NH_3$, of a rose colour, and $RhX_3,5NH_3$, of a yellow colour. Jörgensen, in his researches on these compounds, showed their entire analogy with the cobalt compounds, as was to be expected from the periodic system.

belongs to the type PtX_2, then Gros' salt is of the type PtX_4), is soluble in water, and the elements of nitric acid, but not the chlorine, contained in it are capable of submitting themselves readily to double saline decomposition. Thus, silver nitrate does not enter into double decomposition with the chlorine of Gros' salt.[12a] Most instructive was the circumstance that Gros, by acting on his salt with hydrochloric acid, succeeded in substituting the residue of nitric acid in it by chlorine, and the chlorine thus introduced easily reacted with silver nitrate. Thus, it appeared that Gros' salt contained two varieties of chlorine—one which reacts readily and the other with difficulty. The composition of Gros' first salt is $PtCl_2(NH_3)_4(NO_3)_2$; it may be converted into $PtCl_2(NH_3)_4(SO_4)$, and in general into $PtCl_2(NH_3)_4X_2$.[13]

The salt of Magnus when boiled with a solution of ammonia gives the salt (of Reiset's first base) $PtCl_2(NH_3)_4$, and this, when treated with bromine, forms the salt $PtCl_2Br_2(NH_3)_4$, which has the same composition and reactions as Gros' salt. To Reiset's salts, $PtCl_2(NH_3)_4$, there corresponds a soluble, colourless, crystalline **hydroxide**, $Pt(OH)_2(NH_3)_4$, having the properties of a powerful and very energetic **alkali**; it attracts carbonic anhydride from the atmosphere, precipitates metallic salts like potash, saturates active acids, even sulphuric, forming colourless (with nitric, carbonic, and hydrochloric acids) or yellow (with sulphuric acid) salts of the type $PtX_2(NH_3)_4$.[14] The comparative stability of such

---

[12a] Exactly the same was subsequently observed in certain chromic and cobaltic salts, and the matter must be understood to depend upon the situation of the chlorine with respect to the monatomic elements in the complex compounds.

[13] Subsequently a whole series of such compounds was obtained with various elements in the place of the (non-reacting) chlorine, and all these substituents, like the chlorine, reacted with difficulty, whilst the second portion of the X's introduced into such salts easily underwent reaction. This formed the most inportant reason for the interest which the study of the composition and structure of the platino-ammonium salts presented to many chemists, such as Reiset, Blomstrand, Peyrone, Raeffski, Gerhardt, Buckton, Clève, Thomsen, Jörgensen, Kournakoff, Werner, and others. The salts, $PtX_4,2NH_3$, discovered by Gerhardt, also exhibited several different properties in the two pairs of X's. In the remaining platino-ammonium salts all the X's appear to react alike.

The quality of the X's, retainable in the platino-ammonium salts, may be considerably modified, and they may frequently be wholly or partially replaced by hydroxyl. For example, the action of ammonia on the nitrate of Gerhardt's base, $Pt(NO_3)_4,2NH_3$, in a boiling solution, gradually produces a yellow crystalline precipitate which is nothing else than a **basic hydrate** or **alkali**, $Pt(OH)_4,2NH_3$. It is sparingly soluble in water, but gives soluble salts, $PtX_4,2NH_3$ directly with acids. The stability of this hydroxide is such that potash does not expel ammonia from it, even on boiling, and it does not change below 180°. Similar properties are shown by the hydroxide $Pt(OH)_2,2NH_3$ and the oxide $PtO,2NH_3$ of Reiset's second base. But the hydroxides of the compounds containing $4NH_3$ are particularly remarkable. The presence of ammonia renders them soluble and energetic. The brevity of this work does not permit us, however, to mention many interesting particulars in connection with this subject.

[14] Hydroxides are known corresponding with Gros' salts, which contain one hydroxyl group in the place of that chlorine or haloid which in Gros' salts reacts with difficulty,

compounds, and the existence of many other compounds analogous to them, endow them with a particular chemical interest. Thus

and these hydroxides do not at once show the properties of alkalies, just as the chlorine which stands in the same place does not react distinctly; but still, after the prolonged action of acids, this hydroxyl group is also replaced by acids. Thus, for example, the action of nitric acid on $Pt(NO_3)_2Cl_2,4NH_3$ causes the non-active chlorine to react, but in the product all the chlorine is not replaced by NO_3, but only one half, the other half being replaced by the hydroxyl group:

$$Pt(NO_3)_2Cl_2,4NH_3 + HNO_3 + H_2O = Pt(NO_3)_3(OH),4NH_3 + 2HCl;$$

and this is particularly characteristic, because here the hydroxyl group has not reacted with the acid—an evident sign of the non-alkaline character of this residue. Here it is observable that the reactions of these substances (and probably of many other 'complex' salts) present some resemblance to many of the reactions proper to organic substances where the element of time plays a great part.

To the common properties of the platino-ammonium salts we must add not only their **stability** (feeble acids and alkalies do not decompose them, the ammonia is not evolved by heating, &c.), but also the fact that the ordinary reactions of platinum are concealed in them to as great an extent as those of iron in the ferricyanides. Thus, neither alkalies nor hydrogen sulphide will separate the platinum from them. For example, sulphuretted hydrogen in acting on Gros' salts gives sulphur, removes half the chlorine by means of its hydrogen, and forms salts of Reiset's first base. This may be understood or explained by considering the platinum in the molecule as covered, walled up by the ammonia, or situated in the centre of the molecule, and therefore inaccessible to reagents. On this assumption, however, we should expect to find clearly expressed ammoniacal properties, and this is not the case. Thus, ammonia is easily decomposed by chlorine, whilst in acting on the platino-ammonium salts containing PtX_2 and $2NH_3$ or $4NH_3$, chlorine combines and does not destroy the ammonia; it converts Reiset's salts into those of Gros and Gerhardt. Thus, from $PtX_2,2NH_3$ there is formed $PtX_2Cl_2,2NH_3$, and from $PtX_2,4NH_3$ the salt of Gros' base $PtX_2Cl_2,4NH_3$. This shows that the amount of chlorine which combines is not dependent on the amount of ammonia present, but is due to the basic properties of platinum. Owing to this some chemists suppose the ammonia to be inactive or passive in certain compounds. It appears to me that these relations, these modifications in the usual properties of ammonia and platinum are explained directly by their mutual combination. Sulphur, in sulphurous anhydride, SO_2, and hydrogen sulphide, SH_2, is naturally one and the same, but if we only knew of it in the form of hydrogen sulphide, then, having obtained it in the form of sulphurous anhydride, we should consider its properties as hidden. The oxygen in magnesia, MgO, and that in nitric peroxide, NO_2, are so different that there is no resemblance. We are accustomed to judge the metals by their saline compounds with haloid groups, and ammonia by its compounds with acid substances, and here, in the platino-compounds, if we assume the platinum to be bound to the entire mass of the ammonia—to its hydrogen and nitrogen—we shall understand that both the platinum and ammonia modify their characters. Far more complicated is the question why a portion of the chlorine (and other haloid simple and complex groups) in Gros' salts acts in a different manner from the other portion, and why only half of it acts in the usual way. But this also is not an exclusive case. The chlorine in potassium chlorate or in carbon tetrachloride does not react with metals with the same ease as the chlorine in the salts corresponding with hydrochloric acid. In this case it is united to oxygen and carbon, whilst in the platino-ammonium compounds it is united partly to platinum and partly to the platino-ammonium group. Many chemists, moreover, suppose that a part of the chlorine is united directly to the platinum and the other part to the nitrogen of the ammonia, and thus explain the difference of the reactions; but chlorine united to platinum reacts as well with a silver salt as the chlorine of ammonium chloride, NH_4Cl, or nitrosyl chloride, NOCl, although there is no doubt but that, in this case, there is a union between the chlorine and nitrogen. Hence, Kournakoff (1889) obtained a series of corresponding compounds containing thiocarbamide, CSN_2H_4, in the place of ammonia, $PtCl_2,4CSN_2H_4$, and others corresponding with Reiset's salts. Hydroxylamine

---

it is necessary to explain the absence of a facile reactive capacity in a portion of the chlorine by the conjoint influence of the platinum and the ammonia on it, whilst the other portion may be admitted as being under the influence of the platinum only, and therefore as reacting as in other salts. By admitting a certain kind of stable union in the platino-ammonium grouping, it is possible to imagine that the chlorine does not react with its customary facility, because access to a portion of the atoms of chlorine in this complex grouping is difficult, and the chlorine union is not the same as we usually meet with in the saline compounds of chlorine.

In characterising the platino-ammonium compounds, it is necessary to bear in mind that compounds which already contain PtX_4 do not combine directly with NH_3, and that such compounds as $PtX_4,4NH_3$ only proceed from PtX_2, and therefore it is natural to conclude that those affinities and forces which cause PtX_2 to combine with X_2 also cause it to combine with $2NH_3$. And having the compound $PtX_2,2NH_3$, and supposing that in subsequently combining with Cl_2 it reacts **with those affinities which produce the compounds of platinic chloride, $PtCl_4$, with water,** potassium chloride, potassium cyanide, hydrochloric acid, and the like, we **explain** not only the fact of combination, but also many of the **reactions** occurring in the transition of one kind of platino-ammonium salts into another. Thus, by this means we explain the following facts: (1) that $PtX_2,2NH_3$ combines with $2NH_3$, forming salts of Reiset's first base; (2) and that this compound, $PtX_2,2NH_3,2NH_3$, when heated, or even when boiled in solution, again passes into $PtX_2,2NH_3$ (which resembles the easy disengagement of water of crystallisation, &c.); (3) that $PtX_2,2NH_3$ is capable of absorbing, under the action of the same forces, a molecule of chlorine, $PtX_2,2NH_3,Cl_2$, which it then retains with energy, because it is attracted, not only by the platinum, but also by the hydrogen of the ammonia; (4) that the chlorine held in the compound (of Gerhardt) formed will have a position unusual in salts, which will explain a certain (although very feebly marked) difficulty of reaction; (5) that this does not exhaust the faculty of platinum for further combination (we need only recall the compound $PtCl_4,2HCl,16H_2O$), and that therefore both $PtX_2,2NH_3,Cl_2$ and $PtX_2,2NH_3,2NH_3$ are still capable of combination, whence the latter, with chlorine, gives $PtX_2,2NH_3,2NH_3,Cl_2$, after the type of PtX_4Y_4 (and perhaps higher); (6) that Gros' compounds thus formed are readily re-converted into the salts of Reiset's first base when acted on by reducing agents; (7) that in Gros' salts, $PtX_2,2NH_3(NH_3X)_2$, the newly attached chlorine will react with difficulty with salts of silver, &c., because it is attached both to the platinum and to the ammonia, for both of which it has an attraction; (8) that the faculty for further combination is not even yet exhausted in the type of Gros' salts, and that we actually have a compound of Gros' chlorine salt with platinous chloride and with platinic chloride; the salt $PtSO_4,2NH_3,2NH_3,SO_4$ combines further also with H_2O; (9) that such a faculty of combination with new molecules is naturally more developed in the lower forms of combination than in the higher. Hence the salts of Reiset's first base—for example, $PtCl_2,2NH_3,2NH_3$—both combine with water and give precipitates (soluble in water but not in hydrochloric acid) of double salts with many salts of the heavy metals—for example, with lead chloride, cupric chloride, and also with platinic and platinous chlorides (Buckton's salts). The latter compounds will have the composition $PtCl_2,2NH_3,2NH_3,PtCl_2$—that is, the same composition as the salts of Reiset's second base, with which, however, they cannot be identical. Such an interesting case does actually exist. The first salt, $PtCl_2,4NH_3,PtCl_2$, is green, insoluble in water and in hydrochloric acid, and is known as **Magnus' salt**, and the second, $PtCl_2,2NH_3$, is **Reiset's** yellow and sparingly soluble (in water). They are isomeric (polymeric), and at the same time they easily pass into each other. If ammonia is added to a hot hydrochloric acid solution of platinous chloride, it forms the salt $PtCl_2,4NH_3$, but in the presence of an excess of platinous chloride it gives Magnus' salt. On boiling the latter in ammonia it gives a colourless soluble salt of Reiset's first base, $PtCl_2,4NH_3$, and if this is boiled, and other substances corresponding with ammonia, also give similar compounds. The common properties and composition of such compounds show their great analogy to the cobaltia compounds (especially for ruthenium and iridium), and correspond with the fact that both the platinum metals and cobalt occur in the same (eighth) group.

with water, ammonia is disengaged, and a salt of Reiset's second base, $PtCl_2,2NH_3$, is obtained.

A class of platino-ammonium isomerides (obtained by Millon and Thomsen) is also known. Buckton's salts—for example, the copper salt—were obtained by them from the salts of Reiset's first base, $PtCl_2,4NH_3$, by treatment with a solution of cupric chloride, &c., and therefore, according to our method of expression, Buckton's copper salt will be $PtCl_2,4NH_3,CuCl_2$. This salt is soluble in water, but not in hydrochloric acid. In it the ammonia must be considered as united to the platinum. But if cupric chloride is dissolved in ammonia, and a solution of platinous chloride in ammonium chloride added to it, a violet precipitate is obtained of the same composition as Buckton's salt, which, however, is insoluble in water, but soluble in hydrochloric acid. In this a portion, if not all, of the ammonia must be regarded as united to the copper, and it must therefore be represented as $CuCl_2,4NH_3,PtCl_2$. This form is identical in composition but different in properties (is isomeric) with the preceding salt (Buckton's). The salt of Magnus is intermediate between them, $PtCl_2,4NH_3,PtCl_2$; it is insoluble in water and hydrochloric acid. These and certain other instances of isomeric compounds in the series of the platino-ammonium salts throw a light on the nature of the compounds in question, just as the study of the isomerides of the carbon compounds has served and still serves as the chief cause of the rapid progress of organic chemistry. In conclusion, we may add that (according to the law of substitution) we must necessarily expect all kinds of intermediate compounds between the platino- and analogous ammonia derivatives on the one hand, and the complex compounds of nitrous acid on the other. Perhaps the instance of the reaction of ammonia upon osmic anhydride, OsO_4, observed by Fritsche, Frémy, and others, and more fully studied by Joly (1891), belongs to this class. The latter showed that when ammonia acts upon an alkaline solution of OsO_4, the reaction proceeds according to the equation: $OsO_4 + KHO + NH_3 = OsNKO_3 + 2H_2O$. It might be imagined that in this case the ammonia is oxidised, probably forming the residue of nitrous acid (NO), while the type OsO_4 is deoxidised into OsO_2, and a salt, $OsO(NO)(KO)$, of the type OsX_4 is formed. This salt crystallises well in light yellow octahedra. It corresponds to **osmiamic acid**, $OsO(ON)(HO)$, the anhydride of which, $[OsO(NO)]_2O$, has the composition $Os_2N_2O_5$, which equals $2Os + N_2O_5$ to the same extent as the above-mentioned compound, $PtCO_2$, equals $Pt + CO_2$ (see note 11).

CHAPTER XXIV

COPPER, SILVER, AND GOLD

THAT degree of analogy and difference which exists between iron, cobalt, and nickel repeats itself in the corresponding triads ruthenium, rhodium, and palladium, and osmium, iridium, and platinum. These nine metals form group VIII. of the elements in the periodic system, being the intermediate group between the even elements of the large periods and the uneven ones, among which we know zinc, cadmium, and mercury in group II. Copper, silver, and gold complete [1] this transition, because their properties place them in proximity to nickel, palladium, and platinum on the one hand, and to zinc, cadmium, and mercury on the other. Just as Zn, Cd, and Hg; Fe, Ru, and Os; Co, Rh, and Ir; Ni, Pd, and Pt, resemble each other in many respects, so also do Cu, Ag, and Au. Thus, for example, in atomic weight ($Cu=63{\cdot}6$), and in all its properties, copper stands between $Ni = 59$ and $Zn=65{\cdot}4$. But as the transition from group VIII. to group II., where zinc is situated, cannot be otherwise than through group I., so in copper there are certain properties of the elements of group I. Thus it gives a suboxide, Cu_2O, and salts CuX, like the elements of group I., although at the same time it forms an oxide, CuO, and salts, CuX_2, like nickel and zinc. In the form of the oxide, CuO, and of the salts, CuX_2, copper is analogous to zinc, judging from the insolubility of the carbonates, phosphates, and similar salts, and by the isomorphism and other characters.[2] In the cuprous salts there is undoubtedly a great

---

[1] The perfectly unique position held by copper, silver, and gold in the periodic system of the elements and the degree of affinity which is found between them are all the more remarkable, as nature and practice have long isolated these metals from all others by having employed them—for example, for coinage—and determined their relative importance and value in conformity with the order (silver between copper and gold) of their atomic weights, &c.

[2] Cupric sulphate contains 5 molecules of water, $CuSO_4,5H_2O$, and the isomorphous mixtures with $ZnSO_4,7H_2O$ contain either 5 or 7 equivalents, according to whether copper or zinc predominates (Vol. II., p. 5). If there is a large proportion of copper, and if the mixture contains $5H_2O$, the form of the isomorphous mixture (triclinic) will be isomorphous with cupric sulphate, $CuSO_4,5H_2O$, but if a large amount of zinc (or magnesium, iron, nickel, or cobalt) is present the form (rhombic or monoclinic) will be nearly the same

resemblance to those of silver; thus, for example, silver chloride, AgCl, is characterised by its insolubility and capacity of combining with ammonia, and in this respect cuprous chloride closely resembles it, for it is also insoluble in water, and combines with ammonia and dissolves in it, &c. Its composition is also RCl, the same as AgCl, NaCl, KCl, &c., and silver in many compounds resembles, and is even isomorphous with, sodium; so that this again justifies their being brought together. Silver chloride, cuprous chloride, and sodium chloride crystallise in the regular system. Besides which, the specific heats of copper and silver require that they should have the atomic weights ascribed to them. To the oxides Cu_2O and Ag_2O there are corresponding sulphides, Ag_2S and Cu_2S. These both occur in nature in crystals of the rhombic system, and, what is most important, copper glance contains an isomorphous mixture of them both, and retains the form of copper glance with various proportions of copper and silver, and therefore has the composition R_2S, where $R = Cu, Ag$.

Notwithstanding the resemblance between the atomic compositions of the cuprous, CuX, and silver, AgX, compounds, and that of the compounds of the alkali metals, KX, NaX, there is a considerable degree of difference between these two series of elements. This difference is clearly seen in the fact that the alkali metals belong to those elements which combine with extreme facility with oxygen and decompose water, whilst silver and copper are oxidised with difficulty, form less energetic bases, and do not decompose water, even at moderately high temperatures. Moreover, they displace hydrogen from only very few acids. The difference between them is also seen in the dissimilarity of the properties of many of the corresponding compounds. Thus cuprous oxide, Cu_2O, and silver oxide, Ag_2O, are insoluble in water; the cuprous and silver carbonates, chlorides, and sulphates are also sparingly soluble in water. The oxides of silver and copper are also easily reduced to metal. This difference in properties is in intimate relation with that difference in the density of the metals which exists in this case. The alkali metals belong to the lightest metals, and copper and silver to the heaviest, and therefore the distance between the molecules in these metals is very dissimilar—it is greater for the former than the latter (tables on p. 46, Vol. II.).

Copper is one of the few metals which have long been known in a metallic form. The Greeks and Romans imported copper chiefly from the island of Cyprus—whence its Latin name, *cuprum*. It was known

as that of zinc sulphate, $ZnSO_4,7H_2O$. Supersaturated solutions of each of these salts crystallise in that form and with that amount of water which is contained in a crystal of one or other of the salts brought into contact with the solution (Chap. XIV., note 27).

to the ancients before iron, and was used, especially when alloyed with other metals, for arms and domestic utensils. That copper was known to the ancients will be understood from the facts that it occurs, although rarely, in **a native state**, and that it is easily extracted from its other natural compounds. Among the latter are the oxygen compounds of copper. When ignited with charcoal, they easily give up their oxygen to it, and yield metallic copper; hydrogen also easily takes up the oxygen from copper oxide when heated. Copper occurs in a native state, sometimes in association with other ores, in many parts of the Urals and in Sweden, and in considerable masses in America, especially in the neighbourhood of the great American lakes; and also in Chili, Japan, and China. The oxygen compounds of copper are also of somewhat common occurrence in certain localities. In this respect certain deposits of the Urals are especially famous. The geological period of the Urals (Permian) is characterised by a considerable distribution of copper ores. Copper is met with in the form of **cuprous oxide**, or **suboxide of copper**, Cu_2O, and is then known as **red copper ore**, because it forms red masses which are not infrequently crystallised in the regular system. It is found much more rarely in the state of *cupric oxide*, CuO, and is then called **black copper ore.** The most common of the oxygenised compounds of copper are the **basic carbonates** corresponding with the oxides. That these compounds are undoubtedly of aqueous origin is apparent, not only from the fact that specimens are frequently found of a gradual transition from the metallic, sulphuretted, and oxidised copper into its various carbonates, but also from the presence of water in their composition, and from the laminar, reniform structure which many of them present. In this respect **malachite** is particularly well known: it is used as a green paint and also for ornaments, owing to the diversity of the shades of colour presented by the different layers of deposited malachite. The composition of malachite corresponds with the basic carbonate containing one molecule of cupric carbonate to one of hydroxide: $CuCO_3,CuH_2O_2$. In this form the copper frequently occurs in admixture with various sedimentary rocks, forming large strata, which confirms the aqueous origin of these compounds. There are many such localities in the Perm and other governments bounding the Urals. **Blue carbonate of copper**, or **azurite**, is also often met with in the same localities: it contains the same ingredients as malachite, but in a different proportion, its composition being $CuH_2O_2,2CuCO_3$. Both these substances may be obtained artificially by the action of the alkali carbonates on solutions of cupric salts at various temperatures. These native carbonates are often used for the extraction of copper, especially as they very readily give metallic copper, evolving water and carbonic anhydride when ignited, and leaving the easily reducible cupric oxide. Copper is, however, also often met with in the form of the sulphides. The sulphides of copper generally occur in chemical combination with the sulphides of iron.[3] These copper-sulphur compounds (copper pyrites, $CuFeS_2$, variegated copper ore, Cu_3FeS_3, &c.) generally occur in veins in a rock gangue.

The extraction of copper from its oxide ores does not present any difficulty, because the copper, when ignited with charcoal and melted, is reduced from the impurities which accompany it. This mode of smelting copper ores is carried on in cupola or cylindrical furnaces, fluxes forming a slag being added to the mixture of ore and charcoal. The smelted copper still contains sulphur, iron, and other metallic impurities, from which it is freed by fusion in reverberatory furnaces, with access of air to the surface of the molten metal, as the iron and sulphur are more easily oxidised than the copper. The iron then separates as oxides, which collect in the slag.[4] Copper is frequently

---

[3] Iron pyrites, FeS_2, very often contains a small quantity of copper sulphide (see Chap. XXII., note 2a), and in burning the iron pyrites for sulphurous anhydride the copper oxide remains in the residue, from which the copper is often extracted with profit. For this purpose the whole of the sulphur is not burnt off from the iron pyrites, but a portion is left behind in the ore, which is then slowly ignited (roasted) with access of air. Cupric sulphate is then formed, and is extracted by water; or, as is better and more frequently done, the residue from the roasting of the pyrites is roasted with common salt, and the solution of cupric chloride obtained by lixiviating is precipitated with iron. A far greater amount of copper is obtained from other sulphuretted ores. Among these **copper glance**, Cu_2S, is more rarely met with. It has a metallic lustre, is grey, generally crystalline, and is obtained in admixture with organic matter; so that there is no doubt that its formation is due to the reducing action of the latter on solutions of cupric sulphate. **Variegated copper ore**, which crystallises in octahedra, not infrequently forms an admixture in copper glance: it has a metallic lustre, and is reddish-brown; it has a superficial play of colours, due to oxidation proceeding on its surface. Its composition is Cu_3FeS_3. But the most common and widely distributed copper ore is **copper pyrites**, which crystallises in regular octahedra; it has a metallic lustre, a sp. gr. of 4·0, and a yellow colour. Its composition is $CuFeS_2$. It must be remarked that the sulphurous ores of copper are oxidised in the presence of water containing oxygen in solution, and form cupric sulphate or blue vitriol, which is readily soluble in water. If this water contains calcium carbonate, gypsum and cupric carbonate are formed by double decomposition: $CuSO_4 + CaCO_3 = CuCO_3 + CaSO_4$. Hence copper sulphide in the form of different ores must be considered as the primary product, and the many other copper ores as secondary products, formed by water. This is confirmed by the fact that at the present time the water extracted from many copper mines contains cupric sulphate in solution. From this liquid it is easy to extract cupric oxide by the action of organic matter and various impurities of water. Hence metallic copper is sometimes found in natural products of the modification of copper sulphide, and is probably deposited by the action of organic matter present in the water. Copper salts have been found in the ash of certain plants.

[4] Oxidised ores rich in copper are very rare; the sulphur ores are of more common occurrence, but the extraction of the copper from them is much more difficult. The problem here consists not only in the removal of the sulphur, but also in the removal of the iron combined with the sulphur and copper. This is attained by a whole series of

refined (especially from Fe) by electrolysis. The impure copper forming the anode is immersed in a solution of $CuSO_4$, and the refined copper

operations, after which there sometimes still remains the extraction of the metallic silver which generally accompanies the copper, although in but small quantity. These processes commence with the roasting—i.e., calcination—of the ore with access of air, by which means the sulphur is converted into sulphurous anhydride. It should here be remarked that iron sulphide is more easily oxidised than copper sulphide, and therefore the greater part of the iron in the residue from roasting is no longer in the form of sulphide but of oxide of iron. The roasted ore is mixed with charcoal and silicious fluxes, and smelted in a cupola furnace. The iron then passes into the slag, because its oxide gives an easily fusible mass with the silica, whilst the copper, in the form of sulphide, fuses and collects under the slag. The greater part of the iron is removed from the mass by this smelting. The resultant *coarse metal* is again roasted in order to remove the greater part of the sulphur from the copper sulphide, and to convert the metal into oxide, after which the mass is again smelted. These processes are repeated several times, according to the richness of the ore. During these smeltings a portion of the copper is already obtained in a metallic form, because copper sulphide gives metallic copper with the oxide ($CuS + 2CuO = 3Cu + SO_2$). We shall not describe the furnaces used or the details of this process here, but the above remarks include the explanation of those chemical processes which are accomplished in the various technical operations made use of in the process (for details see works on metallurgy).

Besides the smelting of copper there also exist methods for its extraction from solutions in the **wet way**, as it is called. Recourse is generally had to these methods for poor copper ores. The copper is brought into solution, from which it is separated by means of metallic iron or by other methods (by the action of an electric current). The sulphides are roasted in such a manner that the greater part of the copper is oxidised into cupric sulphate, whilst at the same time the corresponding iron salts are as far as possible decomposed. This process is based on the fact that the copper sulphides absorb oxygen when they are calcined in the presence of air, forming cupric sulphate. The roasted ore is treated with water to which acid is sometimes added, and after lixiviation the resultant solution containing copper is treated either with metallic iron or with milk of lime, which precipitates cupric hydroxide from the solution. Copper oxide ores poor in metal may be treated with dilute acids in order to obtain the copper oxides in solution, from which the copper is then easily precipitated either by iron or, as hydroxide, by lime. According to Hunt and Douglas's method, the copper in the ore is converted by calcination into the cupric oxide, which is brought into solution by the action of a mixture of solutions of ferrous sulphate and sodium chloride; the oxide converts the ferrous chloride into ferric oxide, forming copper chlorides, according to the equation: $3CuO + 2FeCl_2 = CuCl_2 + 2CuCl + Fe_2O_3$. The cupric chloride is soluble in water, whilst the cuprous chloride is dissolved in the solution of sodium chloride, and therefore all the copper passes into solution, from which it is precipitated by iron.

The same American metallurgists give the following wet method for extracting the Ag and Au occurring in many copper ores, especially in sulphur ores: (1) The Cu_2S is first converted into oxide by roasting in a calciner; (2) the CuO is extracted by the dilute sulphuric acid obtained in the fourth process, the Cu then passes into solution, while the Ag, Au, and oxides of iron remain behind in the residue (from which the noble metals may be extracted); (3) a portion of the copper in solution is converted into $CuCl_2$ (and $CaSO_4$ precipitated) by means of the $CaCl_2$ obtained in the fifth process; (4) the mixture of solutions of $CuSO_4$ and $CuCl_2$ is converted into the insoluble CuCl (salt of the suboxide) by the action of the SO_2 obtained by roasting the ore (in the first operation); sulphuric acid is then formed in the solution, according to the equation: $CuSO_4 + CuCl_2 + SO_2 + 2H_2O = 2H_2SO_4 + 2CuCl$; (5) the precipitated CuCl is treated with lime and water, and gives $CaCl_2$ in solution and Cu_2O in the residue; and lastly (6) the Cu_2O is reduced to metallic Cu by carbon in a furnace. According to Crookes's method the impure copper regulus obtained by roasting and smelting the ore is broken up and immersed is deposited on the cathode (certain other impurities, such as Ag, Sb, Sn, Bi, &c., fall as a sediment from the anode).

Copper is characterised by its red colour, which distinguishes it from all other metals. Pure copper, distinguished for its great electro-conductivity (it is employed for conducting electric currents), is soft, and may be beaten out by a hammer at the ordinary temperature, and when hot may be rolled into very thin sheets. Extremely thin leaves of copper transmit a green light. The tenacity of copper is also considerable, and next to iron it is one of the most useful metals in this respect. Copper wire of 1 sq. millimetre in section only breaks under a weight of 30–45 kilograms (according to its purity). The specific gravity of copper is 8·8, unless it contains cavities, due to the fact that molten copper absorbs oxygen from the air, which is disengaged on cooling, thus giving a porous mass whose density is much less. Rolled copper, and also that which is deposited by the electric current, have a comparatively high density. Copper melts at a bright-red heat, about 1050°, although below the temperature at which many kinds of cast iron melt. At a high temperature it is converted into vapour, which communicates a green colour to the flame. Both native copper and that cooled from a molten state crystallise in regular octahedra. Copper is not oxidised in dry air at the ordinary temperature; but when calcined it becomes coated with a layer of oxide, and it does not burn

---

repeatedly in molten lead, which extracts the Ag and Au occurring in the regulus. The regulus is then heated in a reverberatory furnace to run off the lead, and is then smelted for Cu.

Prof. Schtukenberg proposes to extract the copper often present as carbonate in silicious and argillaceous deposits in the Urals by means of the crude acetic acid obtained in the dry distillation of wood. The carbonate is converted into soluble acetate of copper at the ordinary temperature, and the solution when heated deposits metallic copper, owing to the reducing action of the organic matter present in the crude acid. The cheapness and simplicity of this method render it particularly suitable for the Urals, where there are many such deposits (of a greenish colour), and where the dry distillation of wood is carried on on a large scale.

The copper brought into the market often contains small quantities of various impurities. Among these there are generally present iron, lead, silver, arsenic, and sometimes small quantities of oxides of copper. As copper, when mixed with a small amount of foreign substances, loses its tenacity to a certain degree, the manufacture of very thin sheet copper requires the use of Chili copper, which is distinguished for its great softness, and therefore when it is desired to have pure copper, it is best to take thin sheet copper, like that which is used in the manufacture of cartridges. But the purest copper is electrolytic copper—that is, that which is deposited from solution by the action of an electric current.

If the copper contains silver, as is often the case, it is used in gold refineries for the precipitation of silver from its solutions in sulphuric acid. Iron and zinc reduce copper salts, but copper reduces mercury and silver salts. The precipitate contains not only the silver which was previously in solution, but also all that which was in the copper. The silver solutions in sulphuric acid are obtained in the separation of silver from gold by treating their alloys with sulphuric acid, which only dissolves the silver.

even at the highest temperature. When calcined in air, copper forms either the red cuprous oxide or the black cupric oxide, according to the temperature and the quantity of air supplied. In air at the ordinary temperature, copper, as everyone knows, oxidises, turns brown, and becomes coated with a green coating of basic salts, due to the action of the damp air containing carbonic acid. If this action continue for a long time, the copper will become covered with a thick coating of basic carbonate, or the so-called verdigris (the *ærugo nobilis* of ancient statues). This is due to the fact that **copper,** although scarcely capable of oxidising by itself,[5] **in the presence of water and acids**—even very feeble acids, like carbonic acid—**absorbs oxygen from the air and forms salts,** which is a very characteristic property of it (and also of lead).[6]

---

[5] Schützenberger showed that when the basic carbonate of copper is decomposed by an electric current it gives, besides the ordinary copper, an allotropic form which grows on the negative platinum electrode (if its surface be smaller than that of the positive copper electrode), in the form of brittle crystalline growths of sp. gr. 8·1. It differs from ordinary copper by giving, not nitric oxide, but nitrous oxide, when treated with nitric acid, and in being very easily oxidised in air and coated with red shades of colour. It is possible that this is copper hydride, or copper which has occluded hydrogen. Spring (1892) observed that copper reduced from the oxide by hydrogen at the lowest possible temperature was pulverulent, while that reduced from $CuCl_2$ at a somewhat high temperature appeared in bright crystals. The same difference occurs with many other metals, and is probably partly due to the volatility of the metallic chlorides.

[6] This is taken advantage of in practice; for instance, by pouring dilute acids over copper turnings on revolving tables in the preparation of copper salts, such as verdigris, or the basic acetate, $2C_4H_6CuO_4,CuH_2O_2,5H_2O$, which is so much used as a green oil paint (i.e., with boiled linseed or drying oil). The capacity of copper for absorbing oxygen in the presence of acids is so great that it is possible by this means (by taking, for example, thin copper shavings moistened with sulphuric acid) to take up all the oxygen from a given volume of air, and this is even employed for the analysis of air.

The combination of copper with oxygen is aided not only by acids, but also by alkalies, although cupric oxide does not appear to have an acid character. Alkalies do not act on copper except in the presence of air, when they produce cupric oxide, which does not appear to combine with such alkalies as caustic potash or soda. But the **action of ammonia** is particularly distinct (Chap. V., note 2). In the action of a solution of ammonia not only is oxygen absorbed by the copper, but it also acts on the ammonia, and a definite quantity of ammonia is always acted on simultaneously with the passage of the copper into solution. The ammonia is then converted into nitrous acid, according to the reaction: $NH_3 + O_3 = NHO_2 + H_2O$, and the nitrous acid thus formed passes into the state of ammonium nitrite, NH_4NO_2. In this manner three equivalents of oxygen are expended on the oxidation of the ammonia, and six equivalents of oxygen pass over to the copper, forming six equivalents of cupric oxide. The latter does not remain in the state of oxide, but combines with the ammonia.

A strong solution of common salt does not act on copper, but a dilute solution corrodes copper, converting it into the oxychloride—that is, in the presence of air. This action of salt water is evident in those cases where the bottoms of ships are coated with sheet copper. From what has been said above it will be evident that copper vessels should not be employed in the preparation of food, because this contains salts and acids which act on copper in the presence of air, and give copper salts, which are poisonous, and therefore the food prepared in untinned copper vessels may be poisonous. Hence tinned vessels are employed for this purpose—that is, copper vessels coated with a thin layer of tin, on which acid and saline solutions do not act.

Copper does not decompose water, and therefore does not disengage hydrogen from it either at the ordinary or at high temperatures. Nor does copper liberate hydrogen from the oxygen acids ;[6a] these act on it in two ways : they either give up a portion of their oxygen, forming lower grades of oxidation, or else only react in the presence of air. Thus, when nitric acid acts on copper it evolves nitric oxide, the copper being oxidised at the expense of the nitric acid. In the same way copper converts sulphuric acid into the lower grade of oxidation—into sulphurous anhydride, SO_2. In these cases the copper is oxidised to copper oxide, which combines with the excess of acid taken, and therefore forms a cupric salt, CuX_2. Dilute nitric acid does not act on copper at the ordinary temperature ; but when heated it reacts with great ease ; dilute sulphuric acid does not act on copper except in presence of air.

Both the oxides of copper, Cu_2O and CuO, are unacted on by air, and, as already mentioned, they both occur in nature.[6b] However, in the majority of cases copper is obtained in the form of cupric oxide and its salts, and the copper compounds used industrially generally belong to this type. This is due to the fact that the **cuprous compounds absorb oxygen** from the air and pass into cupric compounds. The cupric compounds may serve as the source for the preparation of cuprous oxide, because many reducing agents are capable of deoxidising the oxide into the suboxide. Organic substances are most generally employed for this purpose, and especially saccharine substances, which are able, in the presence of alkalies, to undergo oxidation at the expense of the oxygen of the cupric oxide, and to give acids which combine with the alkali: $2CuO-O=Cu_2O$. In this case the deoxidation of the copper may be carried further and metallic copper obtained, if only the reaction is aided by heat. Thus, for example, a fine powder of metallic copper may be obtained by heat-

---

[6a] In contact with Pt, copper forms a galvanic couple, and is then acted on by HCl, with the evolution of hydrogen.

[6b] Copper gives, besides the cuprous oxide, Cu_2O, and cupric oxide, CuO, two known higher forms of oxidation ; but they have been little investigated, and even their composition is not well known. **Copper dioxide** (CuO_2, or CuO_2,H_2O, perhaps CuO,H_2O_2) is obtained by the action of hydrogen peroxide on cupric hydroxide, when the green colour of the latter is changed to yellow. It is very unstable, and is decomposed even by boiling water, with the evolution of oxygen, whilst the action of acids gives cupric salts, oxygen being also disengaged. A still higher **copper peroxide** is formed by heating a mixture of caustic potash, nitre, and metallic copper to a red heat, and by dissolving cupric hydroxide in solutions of the hypochlorites of the alkali metals. A slight heating of the soluble salt formed is enough for it to be decomposed into oxygen and copper dioxide, which is precipitated. Judging from Frémy's researches, the composition of the copper-potassic salt should be K_2CuO_4. Perhaps this is a compound of the peroxides of potassium, K_2O_2, and of copper, CuO_2.

ing an ammoniacal solution of cupric oxide with caustic potash and grape sugar. But if the reducing action of the saccharine substance proceeds in the presence of a sufficient quantity of alkali in solution, and at not too high a temperature, cuprous oxide is obtained. To see this reaction clearly, it is not sufficient to take any cupric salt, because the alkali necessary for the reaction might precipitate cupric oxide—it is necessary to add previously some substance which will prevent this precipitation. Among such substances, tartaric acid, $C_4H_6O_6$, is one of the best. In the presence of a sufficient quantity of tartaric acid any amount of alkali may be added to a solution of cupric salt without producing a precipitate, because a soluble double salt of cupric oxide and alkali is then formed. If glucose (for instance, honey or molasses) is added to such an alkaline tartaric solution, and the temperature is slightly raised, it first gives a yellow precipitate (this is cuprous hydroxide, CuHO), and then, on boiling, a red precipitate of anhydrous) cuprous oxide. If such a mixture be left for a long time at the ordinary temperature, it deposits well-formed crystals of anhydrous cuprous oxide belonging to the regular system.[7]

---

[7] Colourless solutions of cuprous salts may be obtained by the action of sulphurous or phosphorous acid and similar lower grades of oxidation on the blue solutions of the cupric salts. This is very clearly and easily effected by means of sodium thiosulphate, $Na_2S_2O_3$, which is oxidised in the process. Cuprous oxide can be obtained not only by the deoxidation of cupric oxide, but also directly from metallic copper itself, because the latter, in oxidising at a red heat in air, *first* gives **cuprous oxide**. It is prepared in this manner on a large scale by heating sheet copper rolled into spirals in reverberatory furnaces. Care must be taken that the air is not in great excess, and that the coating of red cuprous oxide formed does not begin to pass into the black cupric oxide. If the oxidised spiral sheet is then unbent, the brittle cuprous oxide falls away from the soft metal. The suboxide obtained in this manner fuses with ease. The cupric oxide, when calcined with finely divided copper (this copper powder may be obtained by many methods—for instance, by immersing zinc in a solution of a copper salt, or by igniting cupric oxide in hydrogen), gives the fusible cuprous oxide: $Cu + CuO = Cu_2O$. Both the native and the artificial cuprous oxides have a sp. gr. of 5·6. It is insoluble in water, and is not acted on by (dry) air. When heated with acids the suboxide forms a solution of a cupric salt and metallic copper; for example, $Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$. However, strong hydrochloric acid does not deposit metallic copper on dissolving cuprous oxide, which is due to the fact that the cuprous chloride formed is soluble in strong hydrochloric acid. Cuprous oxide also dissolves in a solution of ammonia, and in the absence of air gives a colourless solution, which turns blue in the air, absorbing oxygen, owing to the conversion of the cuprous oxide into cupric oxide. The blue solution thus formed may be again reconverted into a colourless solution by immersing a copper strip in it, because the metallic **copper** then **deoxidises the cupric oxide** in the solution **into cuprous oxide**. Cuprous oxide gives red glasses when fused with glass or with salts, forming vitreous alloys. Glass tinted with cuprous oxide is used for ornaments. This may be taken advantage of in testing for copper under the blowpipe by heating the copper compound with borax in the flame of a blowpipe; a red glass is obtained in the reducing flame, and a blue glass in the oxidising flame, owing to the conversion of the cuprous into cupric oxide.

Étard (1882), by passing sulphurous anhydride into a solution of cupric acetate

Cupric chloride, $CuCl_2$, when ignited, gives **cuprous chloride**, CuCl, i.e., the salt corresponding with suboxide of copper, and therefore cuprous chloride is always formed when copper enters into reaction with chlorine at a high temperature. When copper is calcined with mercuric chloride, it forms cuprous chloride and vapours of mercury. The same substance is obtained on heating metallic copper in hydrochloric acid, hydrogen being disengaged; but this reaction only proceeds with finely divided copper, as hydrochloric acid acts very feebly on compact masses of copper, and, in the presence of air, gives cupric chloride. The green solution of cupric chloride is decolorised by metallic copper, cuprous chloride being formed; but this reaction is only accomplished with ease when the solution is very concentrated and when an excess of hydrochloric acid is present to dissolve the cuprous chloride formed. The addition of water to the solution precipitates the cuprous chloride, because it is less soluble in dilute than in strong hydrochloric acid. Many reducing agents which are able to take up half the oxygen from cupric oxide are able, in the presence of hydrochloric acid, to form cuprous chloride. Stannous salts, sulphurous anhydride, alkali sulphites, phosphorous and hypophosphorous acids, and many similar reducing agents act in this manner. The usual method of preparing cuprous chloride consists in passing sulphurous anhydride into a very strong solution of cupric chloride: $2CuCl_2 + SO_2 + 2H_2O = 2CuCl + 2HCl + H_2SO_4$. Cuprous chloride forms colourless cubic crystals which are insoluble in water. It is easily fusible, and even volatile. Fused with soda, CuCl forms crystals of Cu_2O. Under the action of oxidising agents, it passes into the cupric salt, and it absorbs oxygen from moist air, forming cupric oxychloride, Cu_2Cl_2O. **Aqueous ammonia** easily **dissolves** cuprous chloride as well as cuprous oxide; this solution also turns blue on exposure to the air. Thus, an ammoniacal solution of cuprous chloride serves as an excellent absorbent for oxygen; but this solution absorbs not only oxygen, but also certain other gases, for example, carbonic oxide and acetylene.[8]

---

obtained a white precipitate of cuprous sulphite, Cu_2SO_3,H_2O, whilst he obtained the same salt, of a red colour, from the double salt of sodium and copper; but no convincing proofs of isomerism are known in this case.

[8] The solubility of cuprous chloride in ammonia is due to the formation of compounds of the ammonia with the chloride. In a warm solution the compound $NH_3,2CuCl$ is formed, and at the ordinary temperature $CuCl,NH_3$. This salt is soluble in hydrochloric acid, and then forms a corresponding double salt of cuprous chloride and ammonium chloride. By the action of a certain excess of ammonia on a hydrochloric acid solution of cuprous chloride, very well-formed crystals, having the composition $CuCl,NH_3,H_2O$, are obtained. Cuprous chloride is not only soluble in ammonia and hydrochloric acid, but it also dissolves in solutions of certain other salts, for example, sodium chloride, potassium chloride, sodium thiosulphate. All the solutions act as

When copper is oxidised with a considerable quantity of oxygen at a high temperature, or at the ordinary temperature in the presence of acids, and also when it decomposes acids, converting them into lower grades of oxidation (for example, when submitted to the action of nitric and sulphuric acids), it forms **cupric oxide**, CuO, or, in the presence of acids, cupric salts. Copper rust, or that black mass which forms on the surface of copper when it is calcined, consists of cupric oxide. The coating of oxidised copper is very easily separated from the metallic copper, because it is brittle and readily peels off when it is struck or immersed in water. Many copper salts (for instance, the nitrate and carbonate) leave oxide of copper [8a] in the form of friable black powder, after being ignited. If the ignition is carried further, Cu_2O may be formed from the CuO.[8b] Anhydrous cupric oxide

---

very powerful deoxidising substances; for example, it is easy, by means of these solutions, to precipitate gold from its solutions: $AuCl_3 + 3CuCl = Au + 3CuCl_2$.

Among the other compounds corresponding with cuprous oxide, **cuprous iodide**, CuI, is worthy of remark. It is a colourless substance which is insoluble in water and sparingly soluble in ammonia (like silver iodide), but capable of absorbing it, in which respect it resembles cuprous chloride. It is remarkable from the fact that it is exceedingly easily formed from the corresponding cupric compound, CuI_2. A solution of cupric iodide easily decomposes into iodine and cuprous iodide, even at the ordinary temperature, whilst cupric chloride only suffers a similar change on ignition. If a solution of a cupric salt is mixed with a solution of potassium iodide, the cupric iodide formed immediately decomposes into free iodine and cuprous iodide, which separates out as a precipitate. In this case the cupric salt acts in an oxidising manner.

Cuprous oxide, when treated with hydrofluoric acid, gives an insoluble cuprous fluoride, CuF. Cuprous cyanide is also insoluble in water, and is obtained by the addition of hydrocyanic acid to a solution of cupric chloride saturated with sulphurous anhydride. This cuprous cyanide, like silver cyanide, gives a double soluble salt with potassium cyanide. The double cyanide of copper and potassium is tolerably stable in the air, and enters into double decompositions with various other salts, like those double cyanides of iron with which we are already acquainted.

Copper hydride, CuH, also belongs to the number of the cuprous compounds. It was obtained by Würtz by mixing a hot (70°) solution of cupric sulphate with a solution of hypophosphorous acid, H_3PO_2. The addition of the reducing hypophosphorous acid must be stopped when a brown precipitate makes its appearance, and when gas begins to be evolved. When gently heated it disengages hydrogen: it gives cuprous oxide when exposed to the air, burns in a stream of chlorine, and liberates hydrogen with hydrochloric acid: $CuH + HCl = CuCl + H_2$. Zinc, silver, mercury, lead, and many other heavy metals do not form such a compound with hydrogen, either under these circumstances or under the action of hydrogen at the moment of the decomposition of salts by a galvanic current. The greatest resemblance is seen between cuprous hydride and the hydrogen compounds of K, Na, Pd, Ca, and Ba.

[8a] The oxide of copper obtained by igniting the nitrate is frequently used for organic analyses. It is hygroscopic and retains nitrogen (1·5 c.c. per gram) when the nitrate is heated *in vacuo* (Richards and Rogers, 1893).

[8b] Oxide of copper is also capable of dissociating when heated. Debray and Joannis showed that it then disengages oxygen, whose maximum pressure is constant for a given temperature, providing that fusion does not take place (the CuO then dissolves in the molten Cu_2O); and that this loss of oxygen is followed by the formation of suboxide.

is very easily dissolved in acids, forming cupric salts, CuX_2. They are analogous to the salts MgX_2, ZnX_2, NiX_2, FeX_2, in many respects. On adding potassium or ammonium hydroxide to a solution of a cupric salt, it forms a gelatinous blue precipitate of the hydrated oxide of copper, CuH_2O_2, insoluble in water. The resultant precipitate **is redissolved by an excess of ammonia**, and gives a very beautiful **azure-blue** solution, of so intense a colour that the presence of small traces of cupric salts may be discovered by this means.[9] An excess of potassium or sodium hydroxide does not dissolve cupric hydroxide. A hot solution gives a black precipitate of the anhydrous oxide instead of the blue precipitate, and the precipitate of the hydroxide of copper becomes granular and turns black when the solution is heated. This is due to the fact that the blue hydroxide is exceedingly unstable, and when slightly heated it loses the elements of water and gives the black anhydrous cupric oxide: $CuH_2O_2 = CuO + H_2O$.

Cupric oxide fuses at a strong heat, and on cooling forms a heavy crystalline mass, which is black, opaque, and somewhat tenacious. It is a feebly energetic base, so that not only do the oxides of the metals of the alkalies and alkaline earths displace it from its compounds, but

---

[9] Cupric oxide and many of its salts are able to give definite, although unstable, **compounds with ammonia**. This faculty already shows itself in the fact that cupric oxide and its salts dissolve in aqueous ammonia, and also in the fact that salts of copper absorb ammonia gas. If ammonia is added to a solution of any cupric salt, it first forms a precipitate of cupric hydroxide, which then dissolves in an excess of ammonia. The solution thus formed, when evaporated or on the addition of alcohol, frequently deposits crystals of salts containing the elements both of the salt of copper taken and of ammonia. Several such compounds are generally formed. Thus cupric chloride, $CuCl_2$, according to Deherain, forms four compounds with ammonia—namely, with one, two, four, and six molecules of ammonia. The compounds of $CuSO_4$ with 1–5 NH_3 are mentioned in Chap. XXII., note 85.

The solution obtained by the action of aqueous ammonia and air on copper turnings (note 6) is remarkable for its faculty **of dissolving cellulose**, which is insoluble in water, dilute acids, and alkalies. Paper soaked in such a solution acquires the property of not rotting, of being difficultly combustible and waterproof, &c. It has therefore been applied, especially in England, to many practical purposes; for example, to the construction of temporary buildings, for covering roofs, &c. The composition of the substance held in solution is $Cu(HO)_2,4NH_3$.

If dry ammonia gas is passed over cupric oxide heated to 265°, a portion of the oxide of copper gives **copper nitride**, the oxygen of the copper oxide combining with the hydrogen and forming water. The oxide of copper which remains unchanged is easily removed by washing the resultant product with aqueous ammonia. Copper nitride is very stable, and is insoluble; it has the composition Cu_3N (i.e., the copper is here monatomic, as in Cu_2O), and is an amorphous green powder, which is decomposed when strongly ignited, and gives cuprous chloride and ammonium chloride when treated with hydrochloric acid. Like the other nitrides, copper nitride, Cu_3N, has scarcely been investigated. Granger (1892), by heating copper in the vapour of phosphorus, obtained hexagonal prisms of Cu_5P, which passed into Cu_6P (previously obtained by Abel) when heated in nitrogen. Arsenic is easily absorbed by copper, and its presence (like P), even in small quantities, has a great influence upon the properties of copper.

even such oxides as those of lead and silver precipitate it from solutions, which is partially due to these oxides being soluble, although but slightly so, in water. However, cupric oxide, and especially the hydroxide, easily combines with even the least energetic acids, and does not give any compounds with bases; but, on the other hand, **it easily forms basic salts,**[9a] and in this respect outstrips magnesium and recalls the

---

[9a] As a comparatively feeble base, oxide of copper easily forms both basic and double salts. As an instance we may mention the double salts composed of the dichloride, $CuCl_2,2H_2O$, and potassium chloride. The double salt $CuK_2Cl_4,2H_2O$ crystallises from solutions in *blue* plates, but when heated with substances taking up water easily gives *brown* needles, $CuKCl_3$, and at the same time KCl, and this reaction is reversible at 92°, as was shown by Meyerhoffer (1889). With an excess of the copper salt, KCl gives another double salt, $Cu_2KCl_5,4H_2O$, the transition temperature of which is 55°. The instances of equilibria which are encountered in such complex relations are embraced by the **law of phases** given by Gibbs (*Transactions of the Connecticut Academy of Sciences*, 1875–1878, in J. Willard Gibbs's memoir, *On the Equilibrium of Heterogeneous Substances*, and in a more accessible form in the works of H. W. Bakhuis Roozeboom and W. Meyerhoffer, to which sources we refer those desiring information respecting the law of phases). Gibbs calls '**bodies**,' substances (simple or compound) capable of forming homogeneous complexes (for instance, solutions or intercombinations) of a varied composition; a **phase**—a mechanically separable portion of such bodies or of their homogeneous complexes (for instance, a vapour, liquid, or precipitated solid); **perfect equilibrium**—such a state of bodies and of their complexes as is characterised by a constant pressure at a constant temperature even under a change in the amount of one of the component parts (for instance, of a salt in a saturated solution), while an **imperfect equilibrium** is one for which such a change corresponds with a change of pressure (for instance, an unsaturated solution). The law of phases consists in the fact that: n *bodies give only a perfect equilibrium when* $n+1$ *phases participate in that equilibrium*; for example, in the equilibrium of a salt in its saturated solution in water there are two bodies (the salt and water) and three phases, namely, the salt, solution, and vapour, which can be mechanically separated from each other, and to this equilibrium there corresponds a definite pressure. At the same time, n *bodies may occur in* $n+2$ *phases, but only at one definite temperature and one pressure*; a change of one of these may bring about another state (perfect or not—equilibrium stable or unstable). Thus water when liquid at the ordinary temperature offers two phases (liquid and vapour), and is in perfect equilibrium (as also is ice below 0°); but water, ice, and vapour (three phases and only one body) can only be in equilibrium at 0°, and at the ordinary pressure; with a change of t there will remain either only ice and vapour or only liquid water and vapour; whilst with a rise of pressure not only will the vapour pass into the liquid (there again only remain two phases), but also the temperature of the formation of ice will fall (by about 7° per 1,000 atmospheres). The law of phases is applicable to the consideration of the formation of simple or double salts from saturated solutions and to a number of other purely chemical relations. Thus, for example, in the above-mentioned instance, when the bodies are KCl, $CuCl_2$, and H_2O, perfect equilibrium (which here has reference to the solubility) consisting of four phases, corresponds to the following seven cases, considering only the phases (above 0°): $A = CuCl_2,2KCl,2H_2O$; $B = CuCl_2,KCl$; $C = CuCl_2,2H_2O,KCl$, solution and vapour: (1) A + B + solution + vapour; (2) A + C + solution + vapour; (3) A + KCl + solution + vapour; (4) A + B + C + vapour (it follows that B + KCl + solution gives A); (5) A + C + KCl + vapour; (6) B + C + solution + vapour; and (7) B + KCl + solution + vapour. Thus above 92°, A gives B + KCl. The law of phases by bringing complex instances of chemical reaction under simple physical schemes and graphic methods of representation facilitates their study in detail and gives the means of seeking the

oxides of lead or mercury. Hence the hydroxide of copper dissolves in solutions of neutral cupric salts. The cupric salts are generally blue or green, because cupric hydroxide itself is coloured. But some of the salts in the anhydrous state are colourless.[10]

The commonest normal salt is **blue vitriol**, i.e., the normal cupric sulphate. It generally contains five molecules of water of crystallisation, $CuSO_4,5H_2O$. It is formed by heating strong sulphuric acid with copper, sulphurous anhydride being evolved. The same salt is obtained in practice by carefully roasting sulphide ores of copper, and also by the action on them of water containing oxygen in solution : $CuS + O_4 = CuSO_4$. This salt forms a by-product, obtained in gold refineries, when the silver is precipitated from the sulphuric acid solution by means of copper. It is also obtained by pouring dilute sulphuric acid over sheet copper in the presence of air, or by heating cupric oxide or carbonate in sulphuric acid. The crystals of this salt belong to

---

simplest chemical relations dealing with solutions, dissociation, double decompositions, and similar cases, and therefore deserves serious consideration ; but a detailed exposition of this subject must be looked for in works on physical chemistry (see also Chap. XIV., notes 24, 47, and 50 ; Chap. XXII., note 28, &c.).

[10] The normal **cupric nitrate**, $CuN_2O_6,3H_2O$, is obtained as a deliquescent salt of a blue colour (soluble in water and in alcohol) by dissolving copper or cupric oxide in nitric acid. It is so easily decomposed by the action of heat that it is impossible to drive off the water of crystallisation from it before it begins to decompose. During the ignition of the normal salt the cupric oxide formed enters into combination with the remaining undecomposed normal salt, and gives a basic salt, $CuN_2O_6,2CuH_2O_2$. The same basic salt is obtained if a certain quantity of alkali or cupric hydroxide or carbonate is added to the solution of the normal salt, which is even decomposed when boiled with metallic copper, and forms the basic salt as a green powder, which easily decomposes under the action of heat and leaves a residue of cupric oxide. The basic salt, having the composition $CuN_2O_6,3CuH_2O_2$, is nearly insoluble in water.

The normal **carbonate of copper**, $CuCO_3$, occurs in nature, although extremely rarely. If solutions of cupric salts, CuX_2, are mixed with solutions of alkali carbonates, then, as in the case of magnesium, carbonic anhydride is evolved, and basic salts are formed, which vary in composition according to the temperature and conditions of the reaction. By mixing cold solutions, a voluminous blue precipitate is formed, containing an equivalent proportion of cupric hydroxide and carbonate (after standing or heating, its composition is the same as malachite, sp. gr. 3·5) : $2CuSO_4 + 2Na_2CO_3 + H_2O = CuCO_3,CuH_2O_2 + 2Na_2SO_4 + CO_2$. If the resultant blue precipitate is heated in the liquid, it loses water and is transformed into a granular green mass of the composition Cu_2CO_4—i.e., into a compound of the normal salt with anhydrous cupric oxide. This salt of the oxide corresponds with orthocarbonic acid, $C(OH)_4 = CH_4O_4$, where 4H is replaced by 2Cu. On further boiling, this salt loses a portion of the carbonic acid, forming black cupric oxide, so unstable is the compound of copper with carbonic anhydride. Another basic salt which occurs in nature, $CuH_2O_2,2CuCO_3$, is known as *azurite*, or blue carbonate of copper ; it also loses carbonic acid when boiled with water. On mixing a solution of cupric sulphate with sodium sesquicarbonate no precipitate is at first obtained, but after boiling, a precipitate is formed having the composition of malachite. Debray obtained artificial azurite by heating cupric nitrate with chalk. Cupric chloride, $CuCl_2$, crystallises with $2H_2O$ and dissolves easily in water. The addition of a larger proportion of H_2SO_4 to a strong solution of the salt causes the anhydrous $CuCl_2$ to separate out on cooling.

the triclinic system, have a specific gravity of 2·19, are of a beautiful blue colour, and give a solution of the same colour. A hundred parts of water at 0° dissolve 15, at 25° 23, and at 100° about 45 parts of cupric sulphate, $CuSO_4$.[10a] At 100° this salt loses a portion of its water of crystallisation, which it only parts with entirely at a high temperature (220°), and then gives a white powder of the anhydrous sulphate; and the latter, on further calcination, loses the elements of sulphuric anhydride, leaving cupric oxide, like all the cupric salts. The anhydrous (colourless) cupric sulphate is sometimes used for absorbing water: it turns blue in the process. It offers the advantage that it retains both hydrochloric acid and water, but not carbonic anhydride.[11] Cupric sulphate is used for steeping seed corn: this is said to prevent the growth of certain parasites on the plants. In the arts a considerable quantity of cupric sulphate is also used in the preparation of other copper salts—for instance, of certain pigments [11a]—and a particularly

---

[10a] Although sulphate of copper usually crystallises with $5H_2O$, that is, differently from the sulphates of Mg, Fe, and Mn, it is nevertheless perfectly isomorphous with them, as is seen not only in the fact that it gives isomorphous mixtures with them, containing a similar amount of water of crystallisation, but also in the ease with which it forms, like all bases analogous to MgO, double salts, $R_2Cu(SO_4)_2,6H_2O$ (where R = K, Rb, Cs), of the monoclinic system.

A detailed study of the crystalline forms of these salts, made by Tutton (1893) (see Chap. XIII., note 1), showed: (1) that 22 investigated salts of the composition $R_2M(SO_4)_2,6H_2O$, where R = K, Rb, Cs, and M = Mg, Zn, Cd, Mn, Fe, Co, Ni, Cu, present a complete crystallographic resemblance; (2) that in all respects the Rb salts present a transition between the K and Cs salts; (3) that the Cs salts form crystals most easily, and the K salts the most difficultly, and that for the K salts of Cd and Mn it was even impossible to obtain well-formed crystals; (4) that, notwithstanding the closeness of their angles, the general appearance (habit) of the potassium compounds differs very clearly from the Cs salts, while the Rb salts present a distinct transition in this respect; (5) that the angle of inclination of one of the axes to the plane of the two other axes is least in the K salts (angle from 75° to 75° 38′), greatest in the Cs salts (from 72° 52′ to 73° 50′), and in the Rb salts (from 73° 57′ to 74° 42′) intermediate between the two; the replacement of Mg . . . Cu produces but a very small change in this angle; (6) that the other angles and the ratio of the axes of the crystals exhibit a similar variation; and (7) that the variation of the form is thus chiefly determined by the atomic weight of the alkaline metal.

[11] In addition to what has been said (Chap. I., note 65, and Chap. XXII., note 35) respecting the combination of $CuSO_4$ with water and ammonia, we may add that Lachinoff (1893) showed that $CuSO_4,5H_2O$ loses $4\frac{3}{4}H_2O$ at 180°, that $CuSO_4,5NH_3$ also loses $4\frac{3}{4}NH_3$ at 320°, and that only $\frac{1}{4}H_2O$ and $\frac{1}{4}NH_3$ remain in combination with the $CuSO_4$. The last $\frac{1}{4}H_2O$ can only be driven off by heating to 200°, and the last $\frac{1}{4}NH_3$ by heating to 360°. Ammonia displaces water from $CuSO_4,5H_2O$, but water cannot displace the ammonia from $CuSO_4,5NH_3$.

[11a] Commercial blue vitriol generally contains ferrous sulphate. The salt is purified by converting the ferrous salt into a ferric salt by heating the solution with chlorine or nitric acid. The solution is then evaporated to dryness, and the unchanged cupric sulphate extracted from the residue, which will contain the larger portion of the ferric oxide. The remainder will be separated if cupric hydroxide is added to the solution and the latter boiled; the cupric oxide, CuO, then precipitates the ferric oxide, Fe_2O_3, just as it

large quantity is used **in the galvanoplastic process**, which consists in the deposition of copper from a solution of cupric sulphate by the action of a galvanic current, when the metallic copper is deposited on the cathode and takes the shape of the latter. The description of the processes of galvanoplastic art introduced by Jacobi in St. Petersburg forms a part of applied physics, and will not be touched on here, and we shall only mention that, although first introduced for small articles, it is now used for such articles as type moulds (*clichés*), for maps, prints, &c., and also for large statues, and for the deposition of iron, zinc, nickel, gold, silver, &c., on other metals and materials. The beginning of the application of the galvanic current to the practical extraction of metals from solutions has also been established, especially since the dynamo-electric machines of Gramme, Siemens, and others have rendered it possible to cheaply convert the mechanical motion of the steam engine into electric energy. It is to be expected that the application of the electric current, which has long since given such important results in chemistry, will, in the near future, play an important part in technical processes, the example being shown by electric lighting.

The alloys of copper with certain metals, and especially with zinc and tin, are easily formed by directly melting the metals together. They are easily cast into moulds, forged, and worked like copper, whilst they are much more durable in the air, and are therefore frequently used in the arts. Even the ancients used in all cases, not pure copper, but its alloys with tin or different kinds of **bronze** (Chap. XVIII., note 35 ; Chap. XV., note 19b). The alloys of copper with zinc are called **brass** or 'yellow metal.' Brass contains about 32 per cent. of zinc ; generally, however, it does not contain more than 65 per cent. of copper. The remainder is composed of lead and tin, which usually occur, although in small quantities, in brass. Yellow metal contains about 40 per cent. of zinc.[12] The addition of zinc to copper

---

is itself precipitated by silver oxide. But the solution will contain a small proportion of a basic salt of copper, and therefore sulphuric acid must be added to the filtered solution, and the salt allowed to crystallise. Acid salts are not formed, and cupric sulphate itself has an acid reaction on litmus paper.

[12] Among the alloys of copper resembling brass, **delta metal**, invented by A. Dick (London), is largely used (since 1883). It contains 55 per cent. of Cu, and 41 per cent. of Zn, the remaining 4 per cent. being composed of iron (as much as 3½ per cent., which is first alloyed with zinc), or of cobalt, manganese, and certain other metals. The sp. gr. of delta metal is 8·4. It melts at 950°, and then becomes so fluid that it fills up all the cavities in a mould and forms excellent castings. It has a tensile strength of 70 kilos per sq. mm. (gun metal about 20, phosphor bronze about 30). It is very soft especially when heated to 600° ; but after forging and rolling it becomes very hard; it is more difficultly acted upon by air and water than other kinds of brass, and preserves its golden yellow colour for any length of time, especially if well polished. It is used for

changes the colour of the latter to a considerable degree; with a certain amount of zinc the colour of the copper becomes yellow, and with a still larger proportion of zinc, an alloy is formed which has a greenish tint. In those alloys of zinc and copper which contain a larger amount of zinc than of copper, the yellow colour disappears and is replaced by a greyish colour. But when the amount of zinc is diminished to about 18 per cent., the alloy is red and hard, and is called 'tombac.' A contraction takes place in alloying copper with zinc, so that the volume of the alloy is less than the sum of those of the two constituent metals. The zinc volatilises on prolonged heating at a high temperature and the excess of metallic copper remains behind. When heated in the air, the zinc oxidises before the copper, so that all the zinc alloyed with copper may be removed from the copper by this means. An important property of brass containing about 30 per cent. of zinc is that it is soft and malleable in the cold, but becomes somewhat brittle when heated. We may also mention that ordinary copper coins contain, in order to render them hard, tin, zinc, and iron ($Cu=95$ per cent.); that it is now customary to add a small amount of phosphorus to copper and bronze, for the same purpose; and also that copper is added to silver and gold in coining, &c., to render it hard; moreover, in Germany, Switzerland, and Belgium, and other countries, a silver-white alloy (melchior, German silver, &c.), for base coinage, and other purposes, is prepared from brass and nickel (from 10 to 20 per cent. of nickel; 20 to 30 of zinc and 50 to 70 of copper), or directly from copper and nickel, or, more rarely, from an alloy containing silver, nickel, and copper.

Copper, in its cuprous compounds, is so analogous to **silver** that were there no cupric compounds, or if silver gave stable compounds of the higher oxide, AgO, the resemblance would be as close as that between chlorine and bromine, or between zinc and cadmium; but silver compounds corresponding to AgO are quite unknown. Although silver peroxide—which was regarded as AgO, but which Berthelot (1880) recognised as the sesquioxide, Ag_2O_3—is known, it does not form any true salts, and consequently cannot be placed along with cupric oxide. In distinction from copper, silver as a metal does not oxidise under the influence of heat; and its oxides, Ag_2O and Ag_2O_3, easily lose oxygen (see note 8b). Silver does **not oxidise** in

---

making bearings, screw propellers, valves, and many other articles. The alloys containing 45–80 per cent. of Cu crystallise in cubes if slowly cooled (Bi also gives crystals). The alloys approaching Zn_2Cu_3 in their composition exhibit the greatest resistance (under other equal conditions; of purity, forging, rolling, &c.). The addition of 3 per cent. of Al, or 5 per cent. of Sn, improves the quality of brass. Respecting aluminium bronze, see Chap. XVII., Vol. II., p. 99.

air, and is therefore classed among the so-called **noble metals.** It has a white colour, which is much purer than that of any other known metal, especially when the metal is chemically pure. In the arts silver is always used alloyed, because chemically pure silver is so soft that it wears exceedingly easily, whilst when fused with a small amount of copper, it becomes very hard, without losing its colour.[13]

---

[13] There are not many soft metals: lead, tin, copper, silver, iron, and gold are somewhat soft, and potassium and sodium very soft. The metals of the alkaline earths are sonorous and hard, and many other metals are even brittle, especially bismuth and antimony. But the very slight significance which these properties have in determining the fundamental chemical properties of substances (although, however, of immense importance in the practical applications of metals) is seen from the example shown by zinc, which is hard at the ordinary temperature, soft at 100°, and brittle at 200°. At −190° lead is sonorous.

As the value of silver depends exclusively on its purity, and as there is no possibility of telling the amount of impurities alloyed with it from its external appearance, it is customary in most countries to mark an article with the amount of pure silver it contains after an accurately made analysis known as the **assay** of the silver. In France the assay of silver shows the amount of pure silver in 1,000 parts by weight; in Russia the amount of pure silver in 96 parts—that is, the assay shows the number of zolotniks (4·26 grams) of pure silver in one pound (410 grams) of alloyed silver. Russian silver is generally 84 assay—that is, contains 84 parts by weight of pure silver and 12 parts of copper and other metals. French money contains 90 per cent. (in the Russian system this will be 86·4 assay) by weight of silver [English coins and jewellery contain 92·5 per cent. of silver]; the silver rouble is of 83⅓ assay—that is, it contains 86·8 per cent. of silver—and the smaller Russian silver coinage is of 48 assay, and therefore contains 50 per cent. of silver. Silver ornaments and articles are usually made in Russia of 84 and 72 assay. As the alloys of silver and copper, especially after being subjected to the action of heat, are not so white as pure silver, they generally undergo a process known as 'blanching' (or 'pickling') after being worked up. This consists in removing the copper from the surface of the article by subjecting it to a dark-red heat and then immersing it in dilute acid. During the calcination the copper on the surface is oxidised, whilst the silver remains unchanged; the dilute acid then dissolves the copper oxides formed, and pure silver is left on the surface. In order to test a silver article, a portion of its mass must be taken, not from the surface, but at a certain depth. The commonest and most often used method of assay is that known as **cupellation**. It is based on the difference in the oxidisability of copper, lead, and silver. The cupel is a porous cup with thick sides, made by compressing bone ash. The porous mass of bone ash absorbs the fused oxides, especially the lead oxide, which is easily fusible; but it does not absorb the unoxidised metal. The latter collects into a globule under the action of a strong heat in the cupel, and on cooling solidifies into a button, which may then be weighed. Several cupels are placed in a muffle. A muffle is a semi-cylindrical clay vessel, shown in the accompanying drawing. The sides of the muffle are pierced with several orifices, which allow the access of air into it. The muffle is placed in a furnace, where it is strongly

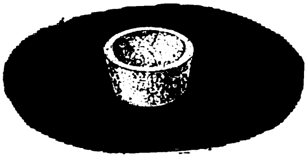


Fig. 108.—Cupel for silver assaying.

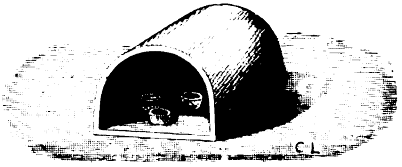


Fig. 109.—Clay muffle.

Silver occurs **in nature**, both in the free state and in certain compounds. Native silver, however, is of rather rare occurrence. A far greater quantity of silver occurs in combination with sulphur, and especially in the form of **silver sulphide**, Ag_2S, with lead sulphide or copper sulphide, or the ores of various other metals. The largest amount of silver is extracted from the lead in which it occurs. If this lead be calcined in the presence of air, it oxidises, and the resultant lead oxide, PbO ('litharge' or 'silberglätte,' as it is called), melts into a mobile liquid, which is easily removed. The silver remains in an unoxidised metallic state.[14] This process is called 'cupellation.'

---

heated. Under the action of the air entering the muffle the copper of the silver alloy is oxidised; but as the oxide of copper is difficultly fusible, a certain quantity of lead is added to the alloy; the lead is also oxidised by the air at the high temperature of the muffle, and gives the very fusible lead oxide. The copper oxide then fuses with the lead oxide, and is absorbed by the cupel, whilst the silver remains as a bright white globule. If the weights of the alloy taken and of the silver left on the cupel are determined, it is possible to calculate the composition of the alloy. Thus the essence of cupellation consists in the separation of the oxidisable metals from silver, which does not oxidise under the action of heat. A more accurate method, based on the precipitation of silver from its solutions in the form of silver chloride, is described in detail in works on analytical chemistry.

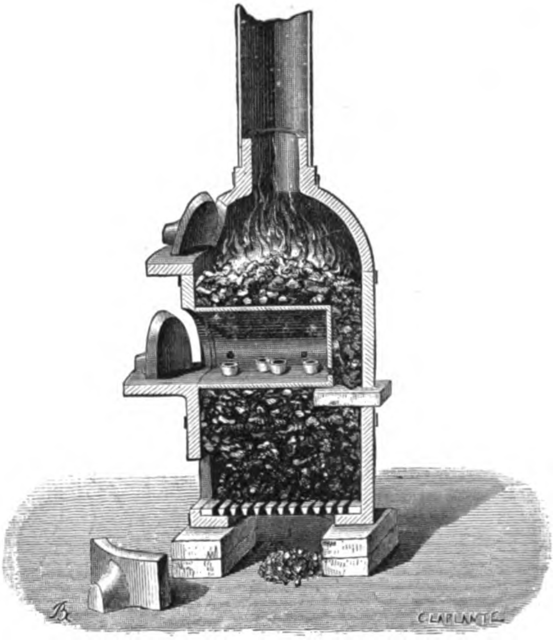


Fig. 110.—Portable muffle furnace.

[14] In America, whence the largest amount of silver is now obtained, ores are worked

Commercial silver generally contains copper, and, more rarely, other metallic impurities also. Chemically **pure silver** is obtained either by

containing not more than $\frac{1}{5}$ per cent. of silver, whilst at $\frac{1}{2}$ per cent. its extraction is very profitable. Moreover, the extraction of silver from ores containing not more than 0·01 per cent. of this metal is sometimes profitable. The majority of the lead smelted from galena contains silver, which is extracted from it. In every case the lead is first extracted in the manner described in Chapter XVIII., and this lead will contain all the silver. Not infrequently other ores of silver are mixed with lead ores in order to obtain an argentiferous lead as the product. The extraction of small quantities of silver from lead is facilitated by the fact (**Pattinson's process**) that molten argentiferous lead in cooling first deposits crystals of pure lead, which fall to the bottom of the cooling vessel, whilst the proportion of silver in the unsolidified mass increases owing to the removal of the crystals of lead (this resembles the separation of ice from salt water). The lead is enriched in this manner until it contains $\frac{1}{400}$ part of silver, and is then subjected to cupellation on a larger scale. According to Parkes's process, zinc is added to the molten argentiferous lead, and the alloy of Pb and Zn, which first separates out on cooling, is collected. This alloy is found to contain all the silver previously contained in the lead. The addition of 0·5 per cent. of aluminium to the zinc (Rossler and Edelman) facilitates the extraction of the Ag from the resultant alloy, besides preventing oxidation; for, after re-melting, nearly all the lead easily runs off (remains fluid), and leaves an alloy containing about 30 per cent. of Ag and about 70 of Zn. This alloy may be used as an anode in a solution of $ZnCl_2$ when the Zn is deposited on the cathode, leaving the silver with a small amount of Pb, &c., behind. The silver can be easily obtained pure by treating it with dilute acids and cupelling.

The ores of silver which contain a larger amount of it are: silver glance, Ag_2S (sp. gr. 7·2); argentiferous copper glance, CuAgS; horn silver or chloride of silver, AgCl; argentiferous grey copper ore; red silver ore, Ag_3SbS_3; polybasite, M_9RS_6 (where $M = Ag, Cu$, and $R = Sb, As$), and argentiferous gold. The latter is the usual form in which gold is found in alluvial deposits and ores. The crystals of gold from the Berezoffsky mines in the Urals contain 90 to 95 of gold and 5 to 9 of silver, and the Altai gold contains 50 to 65 of gold and 36 to 38 of silver. The proportion of silver in native gold varies between these limits in other localities. Silver ores, which generally occur in veins, usually contain native silver and various sulphur compounds. The most famous mines in Europe are in Saxony (Freiberg), which has a yearly output of as much as 26 tons of silver, Hungary and Bohemia (41 tons). In Russia, silver is extracted in the Altai and at Nerchinsk (17 tons). The richest silver mines known are in America, especially in Chili (as much as 70 tons), Mexico (200 tons), and more particularly in the Western States of North America. The richness of these mines may be judged from the fact that one mine in the State of Nevada (Comstock, near Washoe, and the cities of Gold Hill and Virginia), which was discovered in 1859, gave an output of 400 tons in 1866. In place of cupellation, chlorination may also be employed for extracting silver from its ores. The method of chlorination consists in converting the silver in an ore into silver chloride. This is done either by a wet method or by a dry method, in which the ore is roasted with NaCl. When the silver chloride is formed, the extraction of the metal is also done by two methods. The first consists in the silver chloride being reduced to metal by means of iron in rotating barrels, with the subsequent addition of mercury, which dissolves the silver but does not act on the other metals. The mercury holding the silver in solution is distilled, when the silver remains behind. This method is called **amalgamation**. The other method is less frequently used, and consists in dissolving the silver chloride in sodium chloride or in sodium thiosulphate, and then precipitating the silver from the solution. The amalgamation is then carried on in rotating barrels containing the roasted ore mixed with water, iron, and mercury. The iron reduces the silver chloride by taking up the chlorine from it. The technical details of these processes are described in works on metallurgy. The extraction of AgCl by the wet method is carried on (Patera's process) by means of a solution of hyposulphite of sodium, which dissolves AgCl (see note 23), or cupellation or by subjecting ordinary silver to the following treatment. The silver is first dissolved in nitric acid, which converts it and the copper into nitrates, $Cu(NO_3)_2$ and $AgNO_3$; hydrochloric acid is then added to the resultant solution (green, owing to the presence of the cupric salt), which is considerably diluted, with water in order to retain the lead chloride in solution if the silver contained lead. The copper and many other metals remain in solution, whilst the silver is precipitated as silver chloride. The precipitate is allowed to settle, and the liquid is decanted off; the precipitate is then washed and fused with sodium carbonate. A double decomposition then takes place, sodium chloride and silver carbonate being formed; but the latter decomposes into metallic silver, because the silver oxide is decomposed by heat: $Ag_2CO_3 = Ag_2 + O + CO_2$. The silver chloride may also be mixed with metallic zinc, sulphuric acid, and water, and left for some time, when the zinc removes the chlorine from the silver chloride and precipitates the silver as a powder. This finely divided silver is called 'molecular silver.'[15]

Chemically pure silver has an exceedingly pure white colour, and a specific gravity of 10·5. Solid silver is lighter than the molten metal, and therefore a piece of silver floats on the latter. The fusing-point of silver is about 950° C., and at the high temperature attained by the combustion of detonating gas it volatilises.[16] By employing silver reduced from silver chloride by milk sugar and caustic potash, and distilling it, Stas obtained silver purer than that obtained by any other means; in fact, this was perfectly pure silver. The vapour of

---

by lixiviating with a 2 per cent. solution of a double hyposulphite of Na and Cu (obtained by adding $CuSO_4$ to $Na_2S_2O_3$). The resultant solution of AgCl is first treated with soda to precipitate $PbCO_3$, and then with Na_2S, which precipitates the Ag and Au.

[15] There is another practical method which is suitable for separating the silver from the solutions obtained in photography, consisting in precipitating the silver by oxalic acid. In this case the amount of silver in the solution must be known, and 28 grams of oxalic acid dissolved in 400 grams of water must be added for every 60 grams of silver in a litre of solution. A precipitate of silver oxalate, $Ag_2C_2O_4$, is then obtained, which is insoluble in water but soluble in acids. Hence, if the liquid contains any free acid it must be previously neutralised with soda. The resultant precipitate of silver oxalate is dried, mixed with an equal weight of dry sodium carbonate, and thrown into a gently heated crucible. The separation of the silver then proceeds without an explosion, whilst the silver oxalate if heated alone decomposes with explosion.

According to Stas, the best method for obtaining silver from its solutions is by the reduction of silver chloride dissolved in ammonia by means of an ammoniacal solution of cuprous thiosulphate; the silver is then precipitated in a crystalline form. A solution of ammonium sulphite may be used instead of the cuprous salt.

[16] Silver is very malleable and ductile: it may be beaten into leaves 0·002 mm. in thickness. Silver wire may be made so fine that 1 gram is drawn into a wire 2½ kilometres long. In this respect silver is second only to gold. A wire of 2 mm. diameter breaks under a strain of 20 kilograms.

silver has a very beautiful green colour, which is seen when a silver wire is placed in an oxyhydrogen flame.[17]

It has long been known (Wöhler) that when nitrate of silver, $AgNO_3$, reacts as an oxidising agent upon citrates and tartrates, it is able under certain conditions to give either a salt of suboxide of silver (see note 19) or a red solution, or to give a precipitate of metallic silver reduced at the expense of the organic substances. In 1889 Carey Lea, in his researches on this class of reactions, showed that **soluble silver** is here formed, which he called *allotropic silver.* It may be obtained by taking 200 c.c. of a 10 per cent. solution of $AgNO_3$ and quickly adding a mixture (neutralised with NaHO) of 200 c.c. of a 30 per cent. solution of $FeSO_4$ and 200 c.c. of a 40 per cent. solution of sodium citrate. A lilac precipitate is obtained, which is collected on a filter (the precipitate becomes blue) and washed with a solution of NH_4NO_3. It then becomes soluble in pure water, forming a red, perfectly transparent[17a] solution from which the dissolved silver is precipitated on the addition of many soluble foreign bodies. Some of the latter—for instance, NH_4NO_3, alkaline sulphates, nitrates, and citrates —give a precipitate which redissolves in pure water, whilst others—for instance, $MgSO_4$, $FeSO_4$, $K_2Cr_2O_7$, $AgNO_3$, $Ba(NO_3)_2$, and many others—convert the precipitated silver into a new variety, which, although no longer soluble in water, regains its solubility in a solution of borax and is soluble in ammonia. Both the soluble and the insoluble silver

---

[17] In melting, silver **absorbs** a considerable amount of **oxygen**, which is disengaged on solidifying. One volume of molten silver absorbs as much as 22 volumes of oxygen. In solidifying, the silver forms prominences and throws off metal, owing to the evolution of the gas. All these phenomena recall a volcano on a miniature scale (Dumas). Silver which contains a small quantity of copper or gold, &c., does not show this property of dissolving oxygen.

The absorption of oxygen by molten silver is, however, an oxidation, but it is at the same time a phenomenon of solution. One cubic centimetre of molten silver can dissolve twenty-two cubic centimetres of oxygen, which, even at 0°, only weigh 0·03 gram, whilst 1 cubic centimetre of silver weighs at least 10 grams, and therefore it is impossible to suppose that the absorption of the oxygen is attended by the formation of any definite compound of silver and oxygen (about 45 atoms of silver to 1 of oxygen) in any but a dissociated form, and this is the state in which substances in solution must be regarded (Chap. I.).

Le Chatelier showed that at 300° and under 15 atmospheres pressure, silver absorbs so much oxygen that it may be regarded as having formed the compound Ag_4O or a mixture of Ag_2 and Ag_2O. Moreover, silver oxide, Ag_2O, only decomposes at 300° under low pressures, whilst at pressures above 10 atmospheres there is no decomposition at 300° but only at 400°.

Stas showed that silver is oxidised by air in the presence of acids. V. d. Pfordten confirmed this, and showed that an acidified solution of potassium permanganate rapidly dissolves silver in the presence of air.

[17a] Solutions of colloidal substances like soluble silver are really not perfectly transparent, as is shown by polarised light. As a matter of fact there is not much difference between emulsions and such solutions as these.

are rapidly converted into the ordinary grey-metallic variety by sulphuric acid, although nothing is given off in the reaction; the same change takes place on ignition, but in this case CO_2 is disengaged; the latter is formed from the organic substances which remain (to the amount of 3 per cent.) in the modified silver (they are not removed by soaking in alcohol or water). If the precipitated silver is slightly washed and laid in a smooth thin layer on paper or glass, it is seen that the soluble variety is red when moist, and a fine blue colour when dry, whilst the insoluble variety has a blue reflex. Besides these, under special conditions[18] a golden yellow variety may be obtained, which gives a brilliant golden yellow coating on glass; but it is easily converted into the ordinary

---

[18] When solutions of $AgNO_3$, $FeSO_4$, sodium citrate, and NaHO are mixed together in the manner described above, they throw down a precipitate of a beautiful lilac colour; when transferred to a filter paper the precipitate soon changes colour, and becomes dark blue. To obtain the substance as pure as possible it is washed with a 5–10 per cent. solution of ammonium nitrate; the liquid is decanted, and 150 c.c. of water poured over the precipitate. It then dissolves entirely in the water. A small quantity of a saturated solution of ammonium nitrate is added to the solution, and the silver in solution again separates out as a precipitate. These alternate solutions and precipitations are repeated seven or eight times, after which the precipitate is transferred to a filter and washed with 95 per cent. alcohol until the filtrate gives no residue on evaporation. An analysis of the substance so obtained showed that it contained from 97·18 to 97·31 per cent. of metallic silver. Among other methods of preparing soluble silver given by Carey Lea, we may mention the method published by him in 1891. $AgNO_3$ is added to a solution of dextrine in caustic soda or potash; at first a precipitate of brown oxide of silver is thrown down, but the brown colour then changes into a reddish chocolate, owing to the reduction of the silver by the dextrine, and the solution turns a deep red. A few drops of this solution turn water bright red, and give a perfectly transparent liquid. The dextrine solution is prepared by dissolving 40 grams of caustic soda and the same amount of ordinary brown dextrine, in two litres of water. To this solution is gradually added 28 grams of $AgNO_3$ dissolved in a small quantity of water. Many methods were subsequently discovered for preparing the soluble variety of silver and some other metals by the action of different reducing agents. Among these, hydrate of hydrazine (Chap. VI., note 22a) is distinguished for the simplicity and clearness of its action, and was employed for this purpose by Gutbier (1902).

The red solution, described above, after standing several weeks, deposits crystals spontaneously in the form of short black needles and thin prisms, the liquid becoming colourless. This insoluble variety, when rubbed upon paper, has the appearance of bright shining green flakes, which polarise light.

Carey Lea also obtained a golden variety of silver. A solution is prepared containing 200 c.c. of a 10 per cent. solution of nitrate of silver, 200 c.c. of a 20 per cent. solution of Rochelle salt, and 800 c.c. of water. Just as in the previous case the reaction consisted in the reduction of the citrate of silver, so in this case it consists in the reduction of the tartrate, which here first forms a red and then a black precipitate of allotropic Ag, which, when transferred to the filter, appears of a beautiful bronze colour. After washing and drying, this precipitate acquires the lustre and colour peculiar to polished gold, and this is especially remarked where the precipitate comes into contact with glass or china. An analysis of the golden variety gave a percentage composition of 98·750 to 98·749 Ag. Both the insoluble varieties (the blue and the gold) have a different specific gravity from ordinary silver. Whilst that of fused silver is 10·50, and that of finely divided silver 10·62, the specific gravity of the blue insoluble variety is 9·58, and grey metallic state by friction or trituration. There is no doubt[18a] but that there is the same relation between ordinary silver which is perfectly insoluble in water and the varieties of silver obtained by Carey Lea[18b] as there is between quartz and soluble silica or between CuS and As_2S_3 in their ordinary insoluble forms and in the colloidal solutions of their hydrosols (see Chap. I., note 57, and Chap. XVII., note 25a). Here, however, an important step in advance has been made in this respect, that we are dealing with the solution of a simple body, and, moreover, of a metal, i.e., of a particularly characteristic state of matter. And as selenium, boron, gold, and certain other simple bodies have already been obtained in a soluble (colloid) form, and as numerous organic compounds (albuminous substances, gum, cellulose, starch, &c.) and inorganic substances are also known in this form, it might be said that the colloid state (of hydrogels and hydrosols) can be acquired, if not by every substance, at all events by substances of most varied chemical character under particular conditions of their formation from solutions. And this being the case, we may hope that a further study of soluble colloidal compounds, which apparently present various transitions towards emulsions, may throw a new light upon the complex question of solutions, which forms one of the problems of the present epoch of chemical science. Moreover, we may remark that Spring (1890) clearly proved the colloidal state of soluble silver by means of dialysis, as it did not pass through the membrane.

As regards the capacity of silver for chemical reactions, it is remarkable for its small capacity for combination with oxygen and for its considerable energy of combination with sulphur, iodine, and cer-

---

that of the gold variety 8·51. The gold variety passes into ordinary Ag with great ease. This transition may even be remarked on the filter in those places which have accidentally not been moistened with water.

The soluble variety of Ag also passes into the ordinary state with great ease, the heat of conversion being, as Prange showed in 1890, about + 60 calories.

[18a] The opinion of the nature of soluble silver given in the text was first enunciated in the *Journal of the Russian Chemical Society*, February 1, 1890, Vol. XXII., page 73. This view is at the present time generally accepted, and this silver is frequently known as the 'colloidal' variety. I may add that Carey Lea observed the solution of ordinary molecular silver in ammonia without the access of air.

[18b] It is, however, noteworthy that ordinary metallic lead has long been considered soluble in water, that boron has been repeatedly obtained in a brown solution, and that observations upon the development of certain bacteria have shown that the latter die in water which has been for some time in contact with metals. This seems to indicate the passage of small quantities of metals into water (the formation of peroxide of hydrogen may, however, be supposed to have some influence in these cases). And as the colloidal state is shown chiefly by very complex molecules, the cause of the conversion of silver and other simple bodies may perhaps be explained as an aggregation of molecules. Questions of this kind, I think, are awaiting their solution by modern science, although they are unfortunately difficult and have been little studied.

tain kindred non-metals. **Silver does not oxidise** at any temperature, and its oxide, Ag_2O, is decomposed by heat. It is also a very important fact that silver is not oxidised by oxygen either in the presence of alkalies, even at exceedingly high temperatures, or in the presence of acids—at least of dilute acids—which properties render it a very important metal in chemical industry for the fusion of alkalies, and also for many purposes in everyday life; for instance, for making spoons, salt-cellars, &c. Ozone, however, oxidises it. Of all **acids** nitric acid has the greatest **action** on silver. The reaction is accompanied by the formation of oxides of nitrogen and of silver nitrate, $AgNO_3$, which dissolves in water and does not, therefore, hinder the further action of the acid on the metal. The halogen acids, especially hydriodic acid, act on silver, hydrogen being evolved; but this action soon stops, owing to the halogen compounds of silver being insoluble in water and only very slightly soluble in acids; they therefore preserve the remaining mass of metal from the further action of the acid. In consequence of this the action of the halogen acids is only distinctly seen with finely divided silver. Sulphuric acid acts on silver in the same manner that it does on copper, only it must be concentrated and at a higher temperature. Sulphurous anhydride, and not hydrogen, is then evolved; but there is no action at the ordinary temperature, even in the presence of air. Among the various salts, sodium chloride (in the presence of moisture, air, and carbonic acid) and potassium cyanide (in the presence of air) act on silver more decidedly than any others, converting it respectively into silver chloride and a double cyanide.

Although silver does not directly combine with oxygen, still three different degrees of combination with oxygen may be obtained indirectly from the salts of silver. They are all, however, unstable, and decompose into oxygen and metallic silver when ignited. These three oxides of silver have the following composition: **silver suboxide**, Ag_4O,[19] corresponding with the (little investigated) suboxides of the

---

[19] **Silver suboxide**, Ag_4O (or argentous oxide), is obtained from argentic citrate by heating it to 100° in a stream of hydrogen. Water and argentous citrate are then formed, and the latter, although but slightly soluble in water, gives a reddish-brown solution of colloidal silver (note 18), and when boiled this solution becomes colourless and deposits metallic silver, the argentic salt being again formed. Wöhler, who discovered this oxide, obtained it as a black precipitate by adding potassium hydroxide to the above solution of argentous citrate. With hydrochloric acid the suboxide gives a brown compound, Ag_2Cl. Since the discovery of soluble silver the above data cannot be regarded as perfectly trustworthy; it is probable that a mixture of Ag_2 and Ag_2O was being dealt with, so that the actual existence of Ag_4O is now doubtful; but there can be no doubt as to the formation of a subchloride, Ag_2Cl (see note 25), corresponding to the suboxide. The same compound is obtained by the action of light on the higher chloride. Other acids do not combine with silver suboxide, but convert it into an argentic salt and metallic silver. In this respect cuprous oxide

alkali metals ; **silver oxide**, Ag_2O, corresponding with the oxides of the alkali metals and the ordinary salts of silver, AgX ; and **silver peroxide**, AgO,[19a] or, judging from Berthelot's researches, Ag_2O_3. **Silver oxide** is obtained as a brown precipitate (which when dried does not contain water) by adding potassium hydroxide to a solution of a silver salt—for example, of silver nitrate. The precipitate formed seems, however, to be a hydroxide, AgHO, i.e., $AgNO_3 + KHO = KNO_3 + AgHO$, and the formation of the anhydrous oxide, $2AgHO = Ag_2O + H_2O$, may be compared with the formation of the anhydrous cupric oxide by the action of potassium hydroxide on hot cupric solutions. Silver hydroxide decomposes into water and silver oxide, even at low temperatures; at least the hydroxide no longer exists at 60°, but forms the anhydrous oxide, Ag_2O.[19b] Silver oxide is almost insoluble in water; but, nevertheless, it is undoubtedly a rather powerful basic oxide, because it displaces the oxides of many metals from their soluble salts, and saturates such acids as nitric acid, forming with them neutral salts, which do not act on litmus paper.[20] The oxide is distinguished by its great instability when heated, so that it loses all its oxygen when slightly heated. Hydrogen reduces it at about 80°.[20a] The feebleness

---

presents a certain resemblance to these suboxides. But copper forms a suboxide of the composition Cu_4O, which is obtained by the action of an alkaline solution of stannous oxide on cupric hydroxide, and is decomposed by acids into cupric salts and metallic copper. The problems offered by the suboxides, as well as by the peroxides, cannot be considered as fully solved.

[19a] **Silver peroxide**, AgO or Ag_2O_3, is obtained at the anode by the decomposition of a dilute (10 per cent.) solution of silver nitrate by the action of a galvanic current (Ritter). Brittle grey needles with a metallic lustre, which occasionally attain a somewhat considerable size, are then formed. They are insoluble in water and decompose, with the evolution of oxygen, when they are dried and heated up to 150°, and, like lead dioxide, barium peroxide, &c., their action is strongly oxidising. When treated with acids, oxygen is evolved and a salt of the oxide formed. Silver peroxide absorbs sulphurous anhydride and forms silver sulphate. Hydrochloric acid evolves chlorine; ammonia reduces the silver, and is itself oxidised, forming water and gaseous nitrogen. Analyses of the above-mentioned crystals show that they contain silver nitrate and peroxide, and water. According to Berthelot, they possess the composition $4Ag_2O_5,2AgNO_3,H_2O$.

[19b] According to Carey Lea, however, oxide of silver still retains water even at 100°, and only parts with it together with the oxygen. Oxide of silver is used for colouring glass yellow.

[20] The reaction of $Pb(OH)_2$ upon AgHO in the presence of NaHO leads to the formation of a compound of the two oxides, PbO,nAg_2O, from which the oxide of lead cannot be removed by alkalies (Wöhler, Leton). Wöhler, Welch, and others obtained crystalline double salts, R_2AgX_3, by the action of strong solutions of the halogen salts of the alkaline metals, RX, upon AgX, where R = Cs, Rb, K.

[20a] According to Müller, ferric oxide is reduced by hydrogen (see Chap. XXII., note 5) at 295° (into FeO ?), cupric oxide at 140°, Ni_2O_3 at 150°; nickelous oxide, NiO, is reduced to the suboxide, Ni_2O, at 195°, and to nickel at 270°; zinc oxide requires so high a temperature for its reduction that the glass tube in which Müller conducted the experiment did not stand the heat; antimony oxide requires a temperature of 215° for

of the affinity of silver for oxygen is shown by the fact that silver oxide decomposes under the action of light, so that it must be kept in opaque vessels. The silver **salts** are colourless, and decompose when heated, leaving metallic silver if the elements of the acid are volatile.[20b] They have a peculiar metallic taste, and are exceedingly poisonous; the majority of them are acted on by light, especially in the presence of organic substances, which are then oxidised. The alkaline carbonates give a white precipitate of silver carbonate, Ag_2CO_3, which is insoluble in water, but soluble in ammonia and ammonium carbonate. Aqueous ammonia, added to a solution of a normal silver salt, first acts like potassium hydroxide; but the precipitate dissolves in an excess of the reagent, like the precipitate of cupric hydroxide.[21] Silver oxalate and the halogen compounds of silver are insoluble in water; hydrochloric acid and soluble chlorides give, as already repeatedly observed, a white precipitate of silver chloride in solutions of silver salts. Potassium iodide gives a yellowish precipitate of silver iodide. Zinc separates all the silver in a metallic form from solutions of silver salts. Many other metals and reducing agents—for example, organic substances—also reduce silver from the solutions of its salts.

Silver nitrate, $AgNO_3$, is known by the name of **lunar caustic** (or *lapis infernalis*): it is obtained by dissolving metallic silver in nitric acid. If the silver be impure, the resultant solution will contain a mixture of the nitrates of copper and silver. If this mixture is evaporated to dryness and the residue carefully fused at an incipient red heat, all the cupric nitrate is decomposed, whilst the greater part of the silver nitrate remains unchanged. On treating the fused mass with water the latter is dissolved, whilst the cupric

---

its reduction; yellow mercuric oxide is reduced at 130° and the red oxide at 230°; silver oxide at 85°, and platinum oxide even at the ordinary temperature.

[20b] A silica compound, Ag_2OSiO_2 is obtained by fusing $AgNO_3$ with silica. This salt is able to decompose with the evolution of oxygen, leaving $Ag + SiO_2$.

[21] If a solution of a silver salt is precipitated by sodium hydroxide, and aqueous ammonia added drop by drop until the precipitate is completely dissolved, the liquid when evaporated deposits a violent mass of crystalline silver oxide. If moist silver oxide is left in a strong solution of ammonia it gives a black mass, which easily decomposes with a loud explosion, especially when struck. This black substance is called **fulminating silver**. Probably this is a compound like the other compounds of oxides with ammonia, and in exploding, the oxygen of the silver oxide forms water with the hydrogen of the ammonia, which is naturally accompanied by the evolution of heat and formation of gaseous nitrogen, or else, as Raschig states, fulminating silver contains NAg_3 or one of the amides (for instance, $NHAg_2 = NH_3 + Ag_2O - H_2O$). Fulminating silver is also formed when potassium hydroxide is added to a solution of silver nitrate in ammonia. The dangerous explosions which are produced by this compound render it needful that great care be taken when salts of silver come into contact with ammonia and alkalies (see Chap. XVI., note 26).

oxide remains insoluble. If a certain amount of silver oxide is added to the solution containing the nitrates of silver and copper, it displaces all the cupric oxide. In this case it is of course not necessary to take pure silver oxide, but only to pour off some of the solution and to add potassium hydroxide to one portion, and to mix the resultant precipitate of the hydroxides, $Cu(OH)_2$ and AgOH, with the remaining portion.[22] By these methods all the copper can be easily removed and pure silver nitrate obtained (its solution is colourless, while the presence of Cu renders it blue), which may be ultimately purified by crystallisation. It crystallises in colourless, transparent prismatic plates, which are not acted on by air. They are anhydrous. Its sp. gr. is 4·34 and it dissolves in half its weight of water at the ordinary temperature.[22a] The pure salt is not acted on by light, but it easily acts in an oxidising

---

[22] So that we here encounter the following phenomena: Copper displaces silver from the solutions of its salts, and silver oxide displaces copper oxide from cupric salts. Guided by the conceptions enunciated in Chap. XV., we can account for this in the following manner: The atomic volume of silver is 10·3, and that of copper 7·2, of silver oxide 32, and of copper oxide 13. A greater contraction has taken place in the formation of cupric oxide, CuO, than in the formation of silver oxide, Ag_2O, since in the CuO $(13-7=6)$ the volume after combination with the oxygen has increased by very little, whilst the volume of silver oxide is considerably greater than that of the metal it contains $[32-(2\times10{\cdot}3)=11{\cdot}4]$. Hence silver oxide is less compact than cupric oxide, and is therefore less stable; but, on the other hand, there are greater intervals between the atoms in silver oxide than in cupric oxide, and therefore silver oxide is able to give more stable compounds than those of copper oxide. This is verified by the figures and data of their reactions. The specific gravity of copper sulphate in an anhydrous state is 3·53, and that of silver sulphate 5·36; the molecular volume of the former is 45, and of the latter 58. The group SO_3 in the copper occupies, as it were, a volume $45-13=32$, and in the silver salt a volume $58-32=26$; hence a smaller contraction has taken place in the formation of the copper salt from the oxide than in the formation of the silver salt, and consequently the latter should be more stable than the former. Hence silver oxide is able to decompose the salt of copper oxide, whilst with respect to the metals both salts have been formed with an almost identical contraction, since 58 volumes of the silver salt contain 21 volumes of metal (difference$=37$), and 45 volumes of the copper salt contain 7 volumes of copper (difference$=38$). Besides which it must be observed that copper oxide displaces iron oxide, just as silver oxide displaces copper oxide. Silver, copper, and iron, in the form of oxides, displace each other in the above order, but in the form of metals in the reverse order (iron, copper, silver). The cause of this order of the displacement of the oxides lies, amongst other things, in their composition. They have the compositions Ag_2O, Cu_2O_2, Fe_2O_3; the oxide containing a less proportion of oxygen displaces that containing a larger proportion, because the basic character diminishes with the increase of contained oxygen.

Copper also displaces mercury from its salts. It may here be remarked that Spring (1888), on leaving a mixture of dry mercurous chloride and copper for two hours, observed a distinct reduction, which belongs to the category of those phenomena which demonstrate the existence of a mobility of parts (i.e., atoms and molecules) in solid substances.

[22a] The solution of 1 part by weight of $AgNO_3$ requires (according to Kremers) the following amounts of water: At 0°, 0·82 part, at 19·5°, 0·41 part, at 54°, 0·20 part, at 110°, 0·09 part, and, according to Tilden, at 125°, 0·0617 part, and at 133°, 0·0515 part.

manner on the majority of organic substances, which it generally blackens. This is due to the fact that the organic substance is oxidised by the silver nitrate, which is reduced to metallic silver. The latter is thus obtained in a finely divided state, which causes the black stain. This peculiarity is taken advantage of for marking linen. Silver nitrate is for the same reason used **for cauterising wounds** and various growths on the body. Here, again, it acts by virtue of its oxidising capacity in destroying the organic matter, which it oxidises, as is seen from the separation of a coating of black metallic powdery silver on the part cauterised.[22b] From the description of the preparation of silver nitrate it will have been seen that this salt, which fuses at 218°, does not decompose at an incipient red heat; when cast into sticks it is usually employed for cauterising. On further heating, the fused salt undergoes decomposition, forming first silver nitrite and then metallic silver. With ammonia, silver nitrate forms, on evaporation of the solution, colourless crystals containing $AgNO_3,2HN_3$ (Marignac). In general the salts of silver, like cuprous, cupric, zinc, &c., salts, are able to give several compounds with ammonia; for example, silver nitrate in a dry state absorbs three molecules (Rose). The ammonia is generally easily expelled from these compounds by the action of heat.

Nitrate of silver readily forms double salts like $AgNO_3,2NaNO_3$, and $AgNO_3,KNO_3$. Under the action of water and a halogen silver nitrate gives nitric acid (see Vol. I., p. 299, formation of N_2O_5), a halogen salt of silver, and a silver salt of an oxygen acid of the halogen. Thus, for example, a solution of chlorine in water, when mixed with a solution of silver nitrate, gives silver chloride and chlorate. It is here evident that the reaction of the silver nitrate is identical with the reaction of the caustic alkalies, as the nitric acid is all set free and the silver oxide only reacts in exactly the same way as aqueous potash acts on free chlorine. Hence the reaction may be expressed in the following manner: $6AgNO_3 + 3Cl_2 + 3H_2O = 5AgCl + AgClO_3 + 6NHO_3$.

Silver nitrate, like the nitrates of the alkalies, does not contain any water of crystallisation. Moreover, the other salts of silver almost always separate out without any water of crystallisation. The silver salts are further characterised by the fact that they **give neither basic nor acid salts,** owing to which the formation of silver salts generally forms the means of determining the true composition of acids; thus, to any acid H_nX there corresponds a salt Ag_nX—for instance, Ag_3PO_4 (Chap. XIX., note 15).

[22b] It may be remarked that the black stain produced by the reduction of metallic silver disappears under the action of a solution of mercuric chloride or of potassium cyanide, because these salts act on finely divided silver.

Silver gives insoluble and exceedingly stable compounds **with the halogens.** They are obtained by double decomposition with great facility whenever a silver salt comes into contact with halogen salts. Solutions of nitrate, sulphate, and all other kindred salts of silver give a precipitate of silver chloride or iodide with solutions of chlorides and iodides and of the halogen acids, because the halogen salts of silver are insoluble both in water[23] and in other acids. **Silver chloride,** $AgCl$, is then obtained as a white flocculent precipitate, silver bromide forms a yellowish precipitate, and silver iodide has a very distinct yellow colour. These halogen compounds sometimes occur in nature: they are formed by a dry method—by the action of halogen compounds on silver compounds, especially under the influence of heat. Silver chloride easily fuses at 451°. On cooling from a molten state, it forms a somewhat soft hornlike mass which can be cut with a knife and is known as **horn silver.** It volatilises at a higher temperature. Its ammoniacal solution, on the evaporation of the ammonia, deposits crystalline chloride of silver, in octahedra. Bromide and iodide of silver also appear in forms of the regular system, so that in this respect the halogen salts of silver resemble the halogen salts of the alkali metals.[24]

---

[23] Silver chloride is almost completely insoluble in water, but is somewhat soluble in water containing sodium chloride or hydrochloric acid, or other chlorides, and many salts, in solution. Thus at 100°, 100 parts of water saturated with sodium chloride dissolve 0·4 part of silver chloride. Bromide and iodide of silver are less soluble in this respect, as also in regard to other solvents. It should be remarked that **silver chloride dissolves in solutions of ammonia, potassium cyanide, and sodium thiosulphate,** $Na_2S_2O_3$. Silver bromide is almost perfectly analogous to the chloride, but silver iodide is nearly insoluble in a solution of ammonia. Silver chloride even absorbs dry ammonia gas, forming very unstable ammoniacal compounds. When heated, these compounds (Chap. VI., note 8) evolve the ammonia, as they also do under the action of all acids. Silver chloride enters into double decomposition with potassium cyanide, forming a soluble double cyanide, which we shall presently describe. It also forms a soluble double salt, $NaAgS_2O_3$, with sodium thiosulphate.

Silver chloride offers different modifications in the structure of its molecule, as is seen in the variations in the consistency of the precipitate, and in the differences in the action of light, which partially decomposes $AgCl$ (see note 25). Stas and Carey Lea investigated this subject, which has a particular importance in photography, because silver bromide also gives *photo-salts.* There is still much to be discovered in this respect, since Abney showed that perfectly dry $AgCl$ placed in a vacuum in the dark is not in the least acted upon when subsequently exposed to light.

[24] Silver **bromide** and **iodide** (which occur as the minerals bromite and iodite) resemble the chloride in many respects, but the degree of affinity of silver for iodine is greater than that for chlorine and bromine, although less heat is evolved (see note 28a). Deville deduced this fact from a number of experiments. Thus silver chloride, when treated with hydriodic acid, evolves hydrochloric acid, and forms silver iodide. Finely divided silver easily liberates hydrogen when treated with hydriodic acid, and also produces the same decomposition with hydrochloric acid, but in a considerably less degree and only on the surface. The difference between silver chloride and iodide is especially remarkable, since the formation of the former is attended with a greater contraction

Silver chloride may be decomposed, with the separation of silver oxide, by heating it with a solution of an alkali, and if an organic

than that of the latter. The volume of AgCl is 26, of chlorine 27, of silver 10, the sum being 37, so that a contraction has ensued; and in the formation of silver iodide an expansion takes place, for the volumes of Ag and I are 10 and 26 respectively, and that of AgI 39 instead of 36 (density, AgCl, 5·59; AgI, 5·67). The atoms of chlorine have united with the atoms of silver without moving asunder, whilst the atoms of iodine must have moved apart in combining with the silver. It is otherwise with respect to the metal; the distance between its atoms in the metal is 2·2, in silver chloride 3·0, and in silver iodide 3·5; hence its atoms have moved asunder considerably in both cases. It is also very remarkable, as Fizeau observed, that the density of silver iodide increases with a rise of temperature—that is, a contraction takes place when it is heated and an expansion when it is cooled.

In order to explain the fact that in silver compounds the iodide is more stable than the chloride and oxide, Professor N. N. Beketoff, in his *Researches on the Phenomena of Substitutions* (Kharkoff, 1865), proposed the following original hypothesis, which we shall give in almost the words of the author:—In the case of aluminium, the oxide, Al_2O_3, is more stable than the chloride, Al_2Cl_6, or the iodide, Al_2I_6. In the oxide the amount of the metal is to the amount of the element combined with it as 54·8 (Al = 27·3) is to 48, or in the ratio 112 : 100; for the chloride the ratio is 25 : 100; and for the iodide, 7 : 100. In the case of silver the oxide (ratio = 1350 : 100) is less stable than the chloride (ratio = 304 : 100), and the iodide (ratio of the weight of metal to the weight of the halogen = 85 : 100) is the most stable. From these and similar examples it follows that the most stable compounds are those in which the weights of the combined substances are equal. This may be partly explained by the attraction of similar molecules even after they have passed into combination with others. This attraction is proportional to the product of the acting masses. In silver oxide the attraction of Ag_2 for $Ag_2 = 216 \times 216 = 46656$, and the attraction of Ag_2 for $O = 216 \times 16 = 3456$. The attraction of like molecules thus counteracts the attraction of the unlike molecules. The former naturally does not overcome the latter, otherwise there would be a disruption, but it nevertheless diminishes the stability. In the case of an equality or proximity of the magnitude of the combining masses, the attraction of the like parts will counteract the stability of the compound to the least extent; in other words, with an inequality of the combined masses the molecules have an inclination to return to an elementary state, to decompose, which does not exist to such an extent where the combined masses are equal. There is, therefore, a tendency for large masses to combine with large ones, and for small to combine with small ones. Hence $Ag_2O + 2KI$ gives $K_2O + 2AgI$. The influence of an equality of masses on the stability is seen particularly clearly in the effect of a rise of temperature. Argentic, mercuric, auric, and other oxides, composed of unequal masses, are somewhat readily decomposed by heat, whilst the oxides of the lighter metals (like water) are not so easily decomposed. Silver chloride and iodide approach the condition of equality, and are not decomposed by heat. The most stable oxides under the action of heat are those of magnesium, calcium, silicon, and aluminium, since they also approach the condition of equality. For the same reason hydriodic acid decomposes with greater facility than hydrochloric acid. Chlorine does not act on magnesia or alumina, but it acts on lime and silver oxide, &c. This is partially explained by the fact that by considering heat as a mode of motion, and knowing that the atomic heats of the free elements are equal, it must be supposed that the amount of the motion of atoms (their *vis viva*) is constant; and as it is equal to the product of the mass (atomic weight) into the square of the velocity, it follows that the greater the combining weight the smaller will be the square of the velocity; and if the combining weights be nearly equal, the velocities also will be nearly equal. Hence the greater the difference between the weights of the combined atoms the greater will be the difference between their velocities. The difference between the velocities will increase with the temperature, and therefore the temperature of decomposition will be the sooner obtained the greater the original difference—that is, substance is added to the alkali, the chloride can be easily reduced to metallic silver, the silver oxide being reduced in the oxidation of the organic substance. Iron, zinc, and many other metals reduce silver chloride in the presence of water. Cuprous and mercurous chlorides and many organic substances are also able to reduce the silver from chloride of silver. Silver iodide is much more stable than the chloride. The same is also observed with respect to the **action of light** upon moist AgCl. White silver chloride soon acquires a violet colour when exposed to the action of light, and especially under the direct action of the sun's rays. After being acted upon by light it is no longer entirely soluble in ammonia, but leaves metallic silver undissolved, from which it might be assumed that the action of light consisted in the decomposition of the silver chloride into chlorine and metallic silver, and in fact the silver chloride becomes in time darker and darker. Silver bromide and iodide are much more slowly acted on by light, and, according to certain observations, when pure they are even quite unacted on; at least they do not change in weight, so that if they are acted on by light, the change they undergo must be one of a change in the structure of their parts, and not of decomposition, as it is in silver chloride.[24a] The silver chloride under the action of light changes in weight, indicating the formation of a volatile product, and the deposition of metallic silver on dissolving in ammonia shows the loss of chlorine. The change does actually occur under the action of light, but the decomposition does not go as far as into chlorine and silver, but only to the formation of a subchloride of silver, Ag_2Cl,

---

the greater the difference of the weights of the combined substances. The nearer these weights are to each other, the more analogous the motion of the unlike atoms, and, consequently, the more stable the resultant compound.

The instability of cupric chloride and nitric oxide, the absence of compounds of fluorine with oxygen, whilst there are compounds of oxygen with chlorine, the greater stability of the oxygen compounds of iodine than those of chlorine, the stability of boron nitride, and the instability of cyanogen, and a number of similar instances, where, judging from the above argument, one would expect (owing to the closeness of the atomic weights) a stability, show that Beketoff's addition to the mechanical theory of chemical phenomena is still far from sufficient to explain the true relations of affinities. Nevertheless, in his mode of explaining the relative stabilities of compounds, we find an exceedingly interesting treatment of questions of primary importance. Without such efforts it would be impossible to generalise the complex data of experimental knowledge.

Fluoride of silver, AgF, is obtained by dissolving Ag_2O or Ag_2CO_3 in hydrofluoric acid. It differs from the other halogen salts of silver in being soluble in water (1 part of salt in 0·55 of water). It crystallises from its solution in prisms, AgF,H_2O (Marignac), or $AgF,2H_2O$ (Pfaundler), which lose their water *in vacuo*. Güntz (1891), by electrolysing a saturated solution of Ag_2F, obtained *subfluoride of silver*, Ag_2F, which is decomposed by water into $AgF + Ag$. It is also formed by the action of a strong solution of AgF upon finely divided (precipitated) silver.

[24a] The bromogelatine photographic plates now used probably contain the halogen salts of silver in a special colloidal state, as is indicated by what is said in note 25a.

which is of a brown colour, and is easily decomposed into metallic silver and silver chloride, $Ag_2Cl = AgCl + Ag$. This change of the chemical composition and structure of the halogen salts of silver, under the action of light forms the basis of **photography**, because the halogen compounds of silver, after having been exposed to light, give a precipitate of finely divided silver, of a black colour, when treated with reducing agents.[25]

---

[25] In photography these are called 'developers.' The most common developers are: solutions of ferrous sulphate, pyrogallol, ferrous oxalate, hydroxylamine, potassium sulphite, hydroquinone (the last acts particularly well and is very convenient to use), &c. The chemical processes of photography are of great practical and theoretical interest, but it would be impossible in this work to enter into this special branch of chemistry, which has as yet been very little worked out from a theoretical point of view. Nevertheless we shall pause to consider certain aspects of this subject which are of a purely chemical interest, and especially the facts concerning **subchloride of silver**, Ag_2Cl (see note 19), and the *photo-salts* (note 23). There is no doubt that under the action of light $AgCl$ becomes darker in colour, decreases in weight, and probably forms a mixture of $AgCl$, Ag_2Cl, and Ag. But the isolation of the subchloride has only been recently accomplished by Güntz by means of the Ag_2F, discovered by him (see note 24). Many chemists (and among them Hodgkinson) assumed that an oxychloride of silver was formed by the decomposition of $AgCl$ under the action of light. Carey Lea's (1889) and A. Richardson's (1891) experiments showed that the product formed does not, however, contain any oxygen at all, and the change in colour produced by the action of light upon $AgCl$ is most probably due to the formation of Ag_2Cl. This substance was isolated by Güntz (1891) by passing HCl over crystals of Ag_2F (note 24). He also obtained Ag_2I in a similar manner by passing HI, and Ag_2S by passing H_2S over Ag_2F. Ag_2Cl is best prepared by the action of phosphorus trichloride upon Ag_2F. Ag_2Cl has an easily changeable tint, with shades of violet red to violet black. Under the action of light, a similar (isomeric) substance is obtained, which splits up into $AgCl + Ag$ when heated. With potassium cyanide, Ag_2Cl gives $Ag + AgCN + KCl$, whence it is possible to calculate the heat of formation of Ag_2Cl: it has the value 29·7, whilst the heat of formation of $AgCl$ is 29·2, i.e., the reaction $2AgCl = Ag_2Cl + Cl$ corresponds to an absorption of 28·7 major calories. If we admit the formation of such a compound by the action of light, it is evident that the energy of the light is consumed in the above reaction. Carey Lea (1892) subjected $AgCl$, $AgBr$, and AgI to a pressure (of course in the dark) of 8,000 atmospheres, and to trituration with water in a mortar, and observed a change of colour indicating incipient decomposition, which is facilitated under the action of light by the molecular currents set up (Lermantoff, Egoroff). The change of colour of the halogen salts of silver under the action of light, and their faculty of subsequently giving a visible photographic image under the action of 'developers.' must now be regarded as connected with the decomposition of AgX, leading to the formation of Ag_2X, and the different tinted photo-salts must be considered as systems containing such Ag_2X's. Carey Lea obtained photo-salts of this kind not only by the action of light but also in many other ways, which we shall enumerate to prove that they contain the products of an incomplete combination of Ag with the halogens (for the salts Ag_2X must be regarded as such). The photo-salts have been obtained (1) by the imperfect chlorination of silver; (2) by the incomplete decomposition of Ag_2O or Ag_2CO_3 by alternately heating and treating with a halogen acid; (3) by the action of nitric acid or $Na_2S_2O_3$ upon Ag_2Cl; (4) by mixing a solution of $AgNO_3$ with the hydrates of FeO, MnO, and CrO, and precipitating by HCl; (5) by the action of HCl upon the product obtained by the reduction of citrate of silver in hydrogen (note 19); and (6) by the action of milk sugar upon $AgNO_3$ mixed with soda and afterwards acidulating with HCl. All these reactions should lead to the formation of products of imperfect combination with the halogens and give

The insolubility of the halogen compounds of silver forms the basis of many methods used in practical chemistry. Thus, by means of this reaction, it is possible to obtain salts of other acids from a halogen salt of a given metal, for instance, $RCl_2+2AgNO_3=R(NO_3)_2+2AgCl$. The formation of the halogen compounds of silver is very frequently used in the investigation of organic substances; for example, if any product of metalepsis containing iodine or chlorine is heated with a silver salt or silver oxide, the silver combines with the halogen and gives a halogen salt, whilst the elements previously combined with the silver replace the halogen. For instance, ethylene dibromide, $C_2H_4Br_2$, is transformed into ethylene diacetate, $C_2H_4(C_2H_3O_2)_2$, and silver bromide by heating it with silver acetate, $2C_2H_3O_2Ag$. The insolubility of the halogen compounds of silver is still more frequently taken advantage of in determining the amount of silver and halogen in a given solution. If it is required, for instance, to determine the quantity of chlorine present in the form of a metallic chloride in a given solution, a solution of silver nitrate is added to it so long as it gives a precipitate. On **shaking** the liquid, the silver chloride readily settles in the form of heavy flakes. It is possible in this way to precipitate the whole of the chlorine from a solution without adding an excess of silver nitrate, since it can be easily seen whether the addition of a fresh quantity of silver nitrate produces a precipate in the clear liquid. In this manner it is possible to add to a solution containing chlorine as much silver as is required for its entire precipitation, and to calculate the amount of chlorine previously in solution from the amount of the solution of silver nitrate consumed, if the quantity of silver nitrate in this solution has been previously determined.[25a] The atomic propor-

---

photo-salts of a similar diversity of colour to those produced by the action of developers upon the halogen salts of silver after exposure to light.

[25a] In order to determine when the reaction is at an end, a few drops of a solution of K_2CrO_4 are added to the solution of the chloride. Before all the chlorine is precipitated as AgCl, the precipitate (after shaking) is white, since Ag_2CrO_4 with 2RCl gives 2AgCl; but when all the chlorine is thrown down, Ag_2CrO_4 is formed, which colours the precipitate reddish-brown. In order to obtain accurate results the liquid should be neutral to litmus. Although distinguished by its great and frequently made use of insolubility, chloride of silver does not separate out as a visible precipitate, but remains for some time in the form of a colloidal (transparent) solution (hydrosol) when it is formed in the presence of an excess of glue or other colloidal substance (or even a strong solution of sugar, according to Lobry de Bruyn, 1902). This phenomenon is connected with a number of other phenomena—not yet sufficiently generalised—such as the solution of the metals themselves (for instance, soluble silver; see above) and their sulphides. This leads to the thought that the passage of a substance from a liquid soluble state to a solid state, or the new formation of a solid, *always*, apparently, starts from a colloidal state (of a hydrosol), which under other conditions *very quickly* passes into an insoluble crystalline form. Tammann's researches lead to such a conclusion, and questions of this kind are of great interest, and likely to be of great importance in physics and chemistry.

tions and preliminary experiments with a pure salt—for example, with sodium chloride—will give the amount of chlorine from the quantity of silver nitrate. Details of these methods will be found in works on analytical chemistry.[25b]

[25b] **Silver cyanide**, AgCN, is closely analogous to the haloid salts of silver. It is obtained, in similar manner to silver chloride, by the addition of potassium cyanide to silver nitrate. A white precipitate is then formed, which is almost insoluble in boiling water. It is also, like silver chloride, insoluble in dilute acids. However, it is dissolved when heated with nitric acid, and both hydriodic and hydrochloric acids act on it, converting it into silver chloride and iodide. Alkalies, however, do not act on silver cyanide, although they act on the other haloid salts of silver. Ammonia and solutions of the cyanides of the alkali metals dissolve silver cyanide, as they do the chloride. In the latter case double cyanides are formed, for example, $KAgC_2N_2$. This salt is obtained in a crystalline state on evaporating a solution of silver cyanide in potassium cyanide. It is much more stable than silver cyanide itself. It has a neutral reaction, does not change in the air, and does not smell of hydrocyanic acid. Many acids, in acting on a solution of this double salt, precipitate the insoluble silver cyanide. Metallic silver dissolves in a solution of potassium cyanide in the presence of air, with formation of the same double salt and potassium hydroxide, and when silver chloride dissolves in potassium cyanide it forms potassium chloride, besides the salt $KAgC_2N_2$. This double salt of silver is used in silver plating. For this purpose potassium cyanide is added to its solution, as otherwise silver cyanide, and not metallic silver, is deposited by the electric current. If two electrodes—one positive (silver) and the other negative (copper)—are immersed in such a solution, silver will be deposited upon the latter, and the silver of the positive electrode will be dissolved by the liquid, which will thus preserve the same amount of metal in solution as it originally contained. If instead of the negative electrode a copper object is taken, well cleaned from all dirt, the silver will be deposited thereon in an even coating. This, indeed, forms the mode of **silver plating by the wet method**, which is most often used in practice. A solution of one part of silver nitrate in 30 to 50 parts of water, mixed with a sufficient quantity of a solution of potassium cyanide to redissolve the precipitate of silver cyanide formed, gives a dull coating of silver; but if twice as much water is used the same mixture gives a bright coating.

Silver-plating in the wet way has now replaced to a considerable extent the old process of **dry silvering**, because this process, which consists in dissolving silver in mercury and applying the amalgam to the surface of the objects, and then vaporising the mercury, offers the great disadvantage of the poisonous nature of the mercury fumes. Besides these, there is another method of silver plating, based on the direct displacement of silver from its salts by other metals—for example, by copper. The copper reduces the silver from its compounds, and the silver separated is deposited upon the copper. Thus, a solution of silver chloride in sodium thiosulphate deposits a coating of silver upon a strip of copper immersed in it. It is best for this purpose to take pure **silver sulphite**. This is prepared by mixing a solution of silver nitrate with an excess of ammonia and adding a saturated solution of sodium sulphite and then alcohol, which precipitates silver sulphite from the solution. The sulphite and its solutions are very easily decomposed by copper. Metallic iron produces the same decomposition, and iron and steel articles may be very readily silver-plated by means of the thiosulphate solution of silver chloride. Indeed, copper and similar metals may even be silver-plated by means of silver chloride; if the chloride of silver, with a small amount of acid, is rubbed upon the surface of the copper, the latter becomes covered with a coating of silver, which it has reduced.

Silver-plating is not only applicable to metallic objects, but also to glass, china, &c. Glass is silvered for various purposes—for example, glass globes silvered internally are used for ornamentation, and have a mirrored surface. Common looking-glass silvered upon one side forms a mirror which is better than the ordinary mercury mirrors, owing

Accurate experiments, and more especially the **researches of Stas** at Brussels, show the proportion in which silver reacts with metallic chlorides. These researches have led to the determination of the **atomic** or **combining weights** of silver, sodium, potassium, chlorine, bromine, iodine, and other elements, and are distinguished for their model exactitude, and we shall therefore describe them in some detail. As sodium chloride is the chloride most generally used for the precipitation of silver, since it can most easily be obtained in a pure state, we shall here cite the quantitative observations made by Stas for showing the co-relation between the quantities of chloride of sodium and silver which react together. In order to obtain perfectly pure sodium chloride, he took pure rock salt, containing only a small quantity of magnesium and calcium compounds and a small amount of potassium salts. This salt was dissolved in water, and the saturated solution evaporated by boiling. The sodium chloride separated out during the boiling, and the mother liquor containing the impurities was poured off. Alcohol of 65 per cent. strength and platinic chloride were added to the resultant salt in order to precipitate all the potassium and a certain part of the sodium salts. The resultant alcoholic solution, containing the sodium and platinum chlorides, was then mixed with a solution of pure ammonium chloride in order to remove the platinic chloride. After this precipitation the solution was evaporated in a platinum retort, and then separate portions of this purified sodium chloride were collected as they crystallised. The same salt was prepared from sodium sulphate, tartrate, nitrate, and from the platini-chloride, in order to have sodium chloride prepared by different methods and from different sources, and in this manner ten samples of sodium chloride were purified and investigated in their relation to silver. After being dried, weighed quantities of all ten samples of sodium chloride were dissolved in water and mixed with a solution in nitric acid of a weighed quantity of perfectly pure silver. A slightly greater quantity of silver was taken than would be

---

to the truer colours of the image, due to the whiteness of the silver. For optical instruments—for example, telescopes—concave mirrors are now made of silvered glass, which has first been ground and polished into the required form. The **silvering of glass** is based on the fact that silver which is reduced from certain solutions deposits itself uniformly in a perfectly homogeneous and continuous but very thin layer, forming a bright reflecting surface. Certain organic substances have the property of reducing silver in this form. The best known among these are certain aldehydes—for instance, ordinary acetaldehyde, C_2H_4O, which easily oxidises in the air and forms acetic acid, $C_2H_4O_2$. This oxidation also easily takes place at the expense of silver oxide, when a certain amount of ammonia is added to the mixture. The oxide of silver gives up its oxygen to the aldehyde, and the silver reduced from it is deposited in a metallic state in a uniform bright coating. The same action is produced by certain saccharine substances and organic acids, such as tartaric acid, &c.

required for the decomposition of the sodium chloride, and when, after pouring in all the silver solution, the silver chloride had settled, the amount of silver remaining in excess was determined by means of a solution of sodium chloride of known strength. This solution of sodium chloride was added so long as it formed a precipitate. In this manner Stas determined how many parts of sodium chloride correspond to 100 parts by weight of silver. The result of ten determinations was that for the entire precipitation of 100 parts of silver from 54·2060 to 54·2093 parts of sodium chloride were required. The difference is so inconsiderable that it has no perceptible influence on the subsequent calculations. The mean of ten experiments was that 100 parts of silver react with 54·2078 parts of sodium chloride. In order to learn from this the relation between the chlorine and silver, it was necessary to determine the quantity of chlorine contained in 54·2078 parts of sodium chloride, or, what is the same thing, the quantity of chlorine which combines with 100 parts of silver. For this purpose Stas made a series of observations on the quantity of silver chloride obtained from 100 parts of silver. Four syntheses were made by him for this purpose. The first synthesis consisted in the formation of silver chloride by the action of chlorine on silver at a red heat. This experiment showed that 100 parts of silver give 132·841, 132·843, and 132·843 of silver chloride. The second method consisted in dissolving a given quantity of silver in nitric acid and precipitating it by means of gaseous hydrochloric acid passed over the surface of the liquid; the resultant mass was evaporated in the dark to drive off the nitric acid and the excess of hydrochloric acid, and the remaining silver chloride was fused first in an atmosphere of hydrochloric acid gas and then in air. In this process the silver chloride was not washed, and therefore there could be no loss from solution. Two experiments made by this method showed that 100 parts of silver give 132·849 and 132·846 parts of silver chloride. A third series of determinations was also made by precipitating a solution of silver nitrate with a certain excess of gaseous hydrochloric acid. The amount of silver chloride obtained was altogether 132·848. Lastly, a fourth determination was made by precipitating dissolved silver with a solution of ammonium chloride, when it was found that a considerable amount of silver (0·3175) had passed into solution in the washing; for 100 parts of silver there was obtained altogether 132·8417 of silver chloride. Thus, from the mean of seven determinations it appears that 100 parts of silver give 132·8445 parts of silver chloride—that is, that 32·8445 parts of chlorine are able to combine with 100 parts of silver and with that quantity of sodium which is contained in 54·2078 parts of sodium chloride. These observations show that 32·8445 parts of chlorine combine with 100 parts of silver and with 21·3633 parts of sodium. From these figures, expressing the relation between the combining weights of chlorine, silver, and sodium, it would be possible to determine their atomic weights—that is, the combining quantity of these elements with respect to one part by weight of hydrogen or 16 parts of oxygen, if there existed a series of similarly accurate determinations for the reactions between hydrogen or oxygen and one of these elements—chlorine, sodium, or silver. If we determine the quantity of silver chloride which is obtained from silver chlorate, $AgClO_3$, we shall find the relation between the combining weights of silver chloride and oxygen, so that, taking the quantity of oxygen as a constant magnitude, we can learn from this reaction the combining weight of silver chloride, and from the preceding numbers the combining weights of chlorine and silver. For this purpose it was first necessary to obtain pure silver chlorate. This Stas did by acting on silver oxide or carbonate, suspended in water, with gaseous chlorine.[26]

[26] The phenomenon which then takes place is described by Stas as follows, in a manner which is perfect in its clearness and accuracy: if silver oxide or carbonate is suspended in water, and an excess of water saturated with chlorine added, all the silver will be converted into chloride, just as is the case with oxide or carbonate of mercury, and the water then contains, besides the excess of chlorine, only pure hypochlorous acid without the least trace of chloric or chlorous acid. If a stream of chlorine is passed into water containing *an excess of silver oxide* or silver carbonate while the liquid is continually agitated, the reaction is the same as the preceding; silver chloride and hypochlorous acid are formed. But this acid does not long remain in a free state: it gradually acts on the silver oxide and gives **silver hypochlorite**, i.e., $AgClO$. If, after some time, the current of chlorine is stopped but the shaking continued, the liquid loses its characteristic odour of hypochlorous acid, while preserving its energetic decolorising property, because the silver hypochlorite which is formed is easily soluble in water. In the presence of an excess of silver oxide this salt can be kept for several days without decomposition, but it is exceedingly unstable when no excess of silver oxide or carbonate is present. So long as the solution of silver hypochlorite is shaken up with the silver oxide it preserves its transparency and bleaching property; but directly it is allowed to stand, and the silver oxide settles, it becomes rapidly cloudy and deposits large flakes of silver chloride, so that the black silver oxide which had settled becomes covered with the white precipitate. The liquid then loses its bleaching properties and contains in solution **silver chlorate**, i.e., $AgClO_3$, which has a slightly alkaline reaction, owing to the presence of a small amount of dissolved oxide. In this manner the reactions which are consecutively accomplished may be expressed by the equations:

$$6Cl_2 + 3Ag_2O + 3H_2O = 6AgCl + 6HClO;$$
$$6HClO + 3Ag_2O = 3H_2O + 6AgClO;$$
$$6AgClO = 4AgCl + 2AgClO_3.$$

Hence, Stas gives the following method for the preparation of silver chlorate: A slow current of chlorine is caused to act on oxide of silver, suspended in water which is kept in a state of continual agitation. The shaking is continued after the supply of chlorine has been stopped, in order that the free hypochlorous acid should pass into silver hypochlorite, and the resultant solution of the hypochlorite is drawn off from the sediment of the excess of silver oxide. This solution decomposes spontaneously into silver chloride and chlorate. The pure silver chlorate, $AgClO_3$, does not change under the action of light. The salt is prepared for further use by drying it in dry air at 150°. It is neces-

The decomposition of the silver chlorate thus obtained was accomplished by the action of a solution of sulphurous anhydride on it. The salt was first fused by carefully heating it at 243°. The solution of sulphurous anhydride used was one saturated at 0°. Sulphurous anhydride in dilute solutions is oxidised at the expense of silver chlorate, even at low temperatures, with great ease if the liquid is continually shaken, sulphuric acid and silver chloride being formed: $AgClO_3 + 3SO_2 + 3H_2O = AgCl + 3H_2SO_4$. After decomposition, the resultant liquid was evaporated, and the residue of silver chloride weighed. Thus the process consisted in taking a known weight of silver chlorate, converting it into silver chloride, and determining the weight of the latter. The analysis conducted in this manner gave the following results, which, like the preceding, designate the weight in a vacuum calculated from the weights obtained in air. In the first experiment it appeared that 138·7890 grams of silver chlorate gave 103·9795 parts of silver chloride, and in the second experiment that 259·5287 grams of chlorate gave 194·44515 grams of silver chloride, and after fusion 194·4435 grams. The mean result of both experiments, converted into percentages, shows that 100 parts of silver chlorate contain 74·9205 of silver chloride and 25·0795 of oxygen. From this it is possible to calculate the combining weight of silver chloride, because in the decomposition of silver chlorate there are obtained three atoms of oxygen and one molecule of silver chloride: $AgClO_3 = AgCl + 3O$. Taking the weight of an atom of oxygen to be 16, we find from the mean result that the equivalent weight of silver chloride is equal to 143·395. Thus if $O = 16$, $AgCl = 143·395$, and as the preceding experiments show that silver chloride contains 32·8445 parts of chlorine per 100 parts of silver, the weight of the atom of silver[26a] must be 107·94, and that of chlorine 35·45. The weight of the atom of sodium is determined from the fact that 21·3633 parts of sodium combine with 32·8445 parts of chlorine; consequently $Na = 23·05$. This conclusion, arrived at by the analysis of silver chlorate, was verified by means of the analysis of potassium chlorate by decomposing it by heat and determining the weight of the potassium chloride formed, and also by effecting the same decomposition by igniting the chlorate in a stream of hydrochloric acid. The combining weight of potassium

---

sary during drying to prevent the access of any organic matter; this is done by filtering the air through cotton-wool, and passing it over a layer of red-hot copper oxide.

[26a] The results given by Stas's determinations have recently been recalculated and certain corrections have been introduced. We give the average results of van der Plaat's, Thomsen's, and Clark's calculations in the context, as well as in the table given in the Preface, neglecting the doubtful thousandths.

chloride was thus determined, and another series of determinations confirmed the relation between chlorine, potassium, and silver, in the same manner as the relation between sodium, chlorine, and silver was determined above. Consequently, the combining weights of sodium, chlorine, and potassium could be deduced by combining these data with the analysis of silver chlorate and the synthesis of silver chloride. The agreement between the results showed that the determinations made by the last method were perfectly correct, and did not depend in any considerable degree on the methods which were employed in the preceding determinations, as the combining weights of chlorine and silver obtained were the same as before. There was naturally a difference, but so small a one that it undoubtedly depended on the errors incidental to every process of weighing and experiment. The atomic weight of silver was also determined by Stas by means of the synthesis of silver sulphide and the analysis of silver sulphate. The combining weight obtained by this method was 107·920. The synthesis of silver iodide and the analysis of silver iodate gave the figure 107·928. The synthesis of silver bromide with the analysis of silver bromate gave the figure 107·921. The synthesis of silver chloride and the analysis of silver chlorate gave a mean result of 107·937. Hence there is no doubt that the combining weight of silver is at least as much as 107·9—greater than 107·90 and less than 107·95, and probably equal to the mean, 107·92. Stas determined in this manner the combining weights of many other elements, such as lithium, potassium, sodium, bromine, chlorine, iodine, and also nitrogen, for the determination of the amount of silver nitrate obtained from a given amount of silver gives directly the combining weight of nitrogen.

The exhaustive investigations conducted by Stas on the atomic weights of the above-named elements have great significance in the solution of the problem as to whether the atomic weights of the elements can be expressed in whole numbers if the unit taken be the atomic weight of hydrogen. Prout, at the beginning of the last century, stated that this was the case, and held that the atomic weights of the elements are multiples of the atomic weight of hydrogen. The subsequent determinations of Berzelius, Penny, Marchand, Marignac, Dumas, and more especially of Stas, proved this conclusion to be untenable, since a whole series of elements proved to have fractional atomic weights—for example, chlorine, about 35·5. On account of this, Marignac and Dumas stated that the atomic weights of the elements are expressed in relation to hydrogen, either by whole numbers or by numbers with simple fractions of the magnitudes ½ and ¼. But Stas's researches refute this supposition also. Even between the combining weight of hydrogen and oxygen, there is not, so far as is yet known, that simple relation which is required by **Prout's hypothesis,**[27]

---

[27] This hypothesis, for the establishment or refutation of which so many researches have been made, is exceedingly important, and fully deserves the attention which has been given to it. Indeed, if it appeared that the atomic weights of all the elements could be expressed in whole numbers with reference to hydrogen, or if at least they proved to be commensurable with one another, then it could be affirmed with confidence that the elements, with all their diversity, were formed of one material (qualitative) condensed or grouped in various manners into the stable, and, under known conditions, undecomposable groups which we call the atoms of the elements. At first it was supposed that all the elements were nothing else than condensed hydrogen; but when it appeared that the atomic weights of the elements could not be expressed in whole numbers in relation to hydrogen, it was still possible to imagine the existence of a certain material from which both hydrogen and all the other elements were formed. If it should transpire that four atoms of this material form an atom of hydrogen, then the atom of chlorine would present itself as consisting of 142 atoms of this substance, the weight of whose atom would be equal to 0·25. But in this case the atoms of all the elements should be expressed in whole numbers with respect to the weight of the atom of this original material. Let us suppose that the atomic weight of this material is equal to unity, then all the atomic weights should be expressible in whole numbers relatively to this unit. Thus the atom of one element, let us suppose, would weigh m, and that of another n; but, as both m and n must be whole numbers, it follows that the atomic weights of all the elements would be commensurable. But it is sufficient to glance over the results obtained by Stas, and to be assured of their accuracy, especially for silver, in order to entirely destroy, or at least strongly undermine, this attractive hypothesis. We must therefore *refuse our assent* to the doctrine of the building up from a single substance of the elements known to us. This hypothesis is not supported either by any known transformation (for one element has never been converted into another element), or by the commensurability of the atomic weights of the elements. Although the hypothesis of the formation of all the elements from a single substance (for which Crookes has suggested the name 'protyle') is most attractive in its comprehensiveness, it can neither be denied nor accepted for want of sufficient data. Marignac endeavoured, however, to overcome Stas's conclusions as to the incommensurability of the atomic weights by supposing that in his, as in the determinations of all other observers, there were unperceived errors which were quite independent of the mode of observation; for example, silver nitrate might be supposed to be an unstable substance which changes, under the heatings, evaporations, and other processes to which it is subjected in the reactions for the determination of the combining weight of silver. It might be supposed, for instance, that silver nitrate contains some impurity which cannot be removed by any means; it might also be supposed that a portion of the elements of the nitric acid are disengaged in the evaporation of the solution of silver nitrate (owing to the decomposing action of water), and in its fusion, and that we have to deal not with normal silver nitrate, but with a slightly basic salt, or perhaps an excess of nitric acid which cannot be removed from the salt. In this case the observed combining weight will not refer to an actually definite chemical compound, but to some mixture for which there do not exist any perfectly exact combining relations. Marignac upholds this proposition by the fact that the conclusions of Stas and other observers respecting the combining weights determined with the greatest exactitude very nearly agree with the proposition of the commensurability of the atomic weights; for example, the combining weight of silver was shown to be equal to 107·92, so that it only differs by 0·08 from the whole number 108, which is sometimes accepted for silver. The combining weight of iodine proved to be equal to 126·85—that is, it differs from 127 by 0·15. The combining weights of sodium, nitrogen, bromine, chlorine, and lithium are still nearer to the whole or round numbers, which are sometimes accepted. But Marignac's proposition will hardly bear criticism. Indeed, if we express the combining weights of the elements determined by Stas in relation to hydrogen, the approximation of these weights to whole numbers

i.e., taking $0 = 16$, the atomic weight of hydrogen is equal not to 1 but to a greater number not less than 1·007 and not more than 1·009 or, say, 1·008. Such a conclusion arrived at by direct experiment cannot but be regarded as having greater weight than Prout's supposition (hypothesis) that the atomic weights of the elements are in multiple

disappears, because one part of hydrogen does not in reality combine with 16 parts of oxygen, but with 15·87 parts, and therefore we shall obtain, taking $H = 1$, not the above-cited figures, but for silver 107·12, for bromine 79·36—magnitudes which are still further removed from whole numbers. Besides which, if Marignac's proposition were true, the combining weight of silver determined by one method—e.g., by the analysis of silver chlorate combined with the synthesis of silver chloride—would not agree well with the combining weight determined by another method—e.g., by means of the analysis of silver iodate and the synthesis of silver iodide. If in one case a basic salt could be obtained, in the other case an acid salt might be obtained. Then the analysis of the acid salt would give different results from that of the basic salt. Thus Marignac's arguments cannot serve as a support for the vindication of Prout's hypothesis.

In conclusion, I think it will not be out of place to cite the following passage from a paper I read before the Chemical Society of London in 1889 (Appendix II.), referring to the hypothesis of the complexity of the elements recognised in chemistry, owing to the fact that many have endeavoured to apply the periodic law to the justification of this idea, dating from a remote antiquity, when it was found convenient to admit the existence of many gods but only one matter.

'When we try to explain the origin of the idea of a unique primary matter, we easily trace that, in the absence of deductions from experiment, it derives its origin from the scientifically philosophical attempt at discovering some kind of unity in the immense diversity of individualities which we see around. In classical times such a tendency could only be satisfied by conceptions about the immaterial world. As to the material world, our ancestors were compelled to resort to some hypothesis, and they adopted the idea of unity in the formative material, because they were not able to evolve the conception of any other possible unity in order to connect the multifarious relations of matter. Responding to the same legitimate scientific tendency, natural science has discovered throughout the universe a unity of plan, a unity of forces, and a unity of matter; and the convincing conclusions of modern science compel everyone to admit these kinds of unity. But while we admit unity in many things, we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere. It was said of old "Give us a fulcrum and it will become easy to displace the earth." So also we must say, "Give us something that is individualised, and the apparent diversity will be easily understood." Otherwise, how could unity result in a multitude ?

'After a long and painstaking research, natural science has discovered the individualities of the chemical elements, and is therefore now capable, not only of analysing, but also of synthesising ; it can understand and grasp generality and unity, as well as the individualised and multifarious. The general and universal, like time and space, like force and motion, vary uniformly. The uniform admit of interpolations, revealing every intermediate phase ; but the multitudinous, the individualised—such as ourselves, or the chemical elements, or the members of a peculiar periodic function of the elements, or Dalton's multiple proportions—is characterised in another way. We see in it, side by side with a general connecting principle—leaps, breaks of continuity, points which escape from the analysis of the infinitely small—an absence of complete intermediate links. Chemistry has found an answer to the question as to the causes of multitudes, and while retaining the conception of many elements, all submitted to the discipline of a general law, it offers an escape from the Indian Nirvana—the absorption in the universal—replacing it by the individualised. However, the place for individuality is so limited by the all-grasping, all-powerful universal that it is merely a point of support for the understanding of multitude in unity.'

proportion to each other, which would give reason for surmising (but not asserting) a complexity of nature in the elements, and their common origin from a single primary material, and for expecting their mutual conversion into each other. All such ideas and hopes must now, thanks more especially to Stas, be placed in a region void of any experimental support whatever, and therefore not subject to the discipline of the positive data of science.

Among the platinum metals, ruthenium, rhodium, and palladium, by their atomic weights and properties, approach silver, just as iron and its analogues (cobalt and nickel) approach copper in all respects. **Gold** stands in exactly the same position in relation to the heavy platinum metals, osmium, iridium, and platinum, as copper and silver do to the two preceding series. The atomic weight of gold is nearly equal to their atomic weights:[28] it is dense like these metals. It also gives various degrees of oxidation, which are feeble, in both a basic and an acid sense. Whilst near to osmium, iridium, and platinum, gold at the same time is able, like copper and silver, to form compounds which answer to the type RX—that is, oxides of the composition R_2O. Cuprous chloride, CuCl, silver chloride, AgCl, and aurous chloride, AuCl, are substances which are very much alike in their physical and chemical properties.[28a] They are insoluble in water,

---

[28] It might be expected from the periodic law and analogies with the series iron, cobalt, nickel, copper, zinc, that the atomic weights of the elements of the series osmium, iridium, platinum, gold, mercury, would rise in this order, and at the time of the establishment of the periodic law (1869), the determinations of Berzelius, Rose, and others gave the following values for the atomic weights: Os = 200, Ir = 197, Pt = 198, Au = 196, Hg = 200. The fulfilment of the expectations of the periodic law was given in the first place by the fresh determinations (Seubert, Dittmar, and Arthur) of the atomic weight of platinum, which proved to be nearly 195, if O = 16 (as Marignac, Brauner, and others propose); in the second place, by the fact that Seubert proved that the atomic weight of osmium is really less than that of platinum, and approximately Os = 191; and, in the third place, by the fact that after the researches of Krüss, Thorpe, and Laurie there was no doubt that the atomic weight of gold is greater than that of platinum—namely, nearly 197.

[28a] In Chap. XXII., note 40, we gave the thermal data for certain of the compounds of copper of the type CuX_2; we shall now cite certain data for the cuprous compounds of the type CuX, which present an analogy to the corresponding compounds AgX and AuX, some of which were investigated by Thomsen in his classical work, *Thermochemische Untersuchungen* (vol. iii., 1883). The data are given in the same manner as in the above-mentioned note:

R =	Cu	Ag	Au
R + Cl	+ 33	+ 29	+ 6
R + Br	+ 25	+ 23	0
R + I	+ 16	+ 14	− 6
R_2 + O	+ 41	+ 6	− ?

Thus, we see in the first place that gold, which possesses a much smaller affinity than Ag, evolves far less heat than an equivalent amount of copper, giving the corresponding but dissolve in hydrochloric acid and ammonia, in potassium cyanide, sodium thiosulphate, &c. Just as copper forms a link between the iron metals and zinc, and as silver unites the light platinum metals with cadmium, so also gold presents a transition from the heavy platinum metals to mercury. Copper gives saline compounds of the types CuX and CuX_2, silver of the type AgX, whilst gold, besides compounds of the type AuX, very easily and most frequently forms those of the type $AuCl_3$. The compounds of this type frequently pass into those of the lower type, just as PtX_4 passes into PtX_2, and the same is observable in the elements which, in their atomic weights, follow gold. Mercury gives HgX_2 and HgX, thallium TlX_3 and TlX, and lead PbX_4 and PbX_2. On the other hand, gold in a qualitative respect differs from silver and copper in the **extreme ease** with which all its compounds are **reduced to metal** by many means. This is accomplished not only by many reducing agents, but also by the action of heat. Thus, its chlorides and oxides lose their chlorine and oxygen when heated, and, if the temperature is sufficiently high, these elements are entirely expelled and metallic gold alone remains. Its compounds, therefore, act as oxidising agents.[29]

In nature gold occurs in the primary and chiefly in quartzose rocks, and especially in quartz veins, as in the Urals (at Berezoffsk), in Australia, and in California. The native gold is extracted from these rocks by subjecting them to a mechanical treatment consisting of

---

compound, and in the second place that the combination of copper with one atom of oxygen disengages more heat than its combination with a halogen, whilst with silver the reverse is the case. This is connected with the fact that Cu_2O is more stable under the action of heat than Ag_2O.

[29] Heavy atoms and molecules, although they may present many points of analogy, are more easily isolated; thus $C_{16}H_{32}$, although, like C_2H_4, it combines with Br_2, and has a similar composition, yet reacts with much greater difficulty than C_2H_4, and in this it resembles gold. The heavy atoms and molecules are, as it were, inert, and already saturated by themselves. Gold in its higher degree of oxidation, Au_2O_3, presents feeble basic properties and weakly developed acid properties, so that this oxide of gold, Au_2O_3, may be referred to the class of feeble acid oxides, like platinic oxide. This is not the case with the highest known oxides of copper and silver. But in the lower grade of oxidation, aurous oxide, Au_2O, gold, like silver and copper, presents basic properties, although they are not very pronounced. In this respect it stands very close in its properties, although not in its types of combination (AuX and AuX_3), to platinum (PtX_2 and PtX_4) and its analogues.

As yet the general chemical characteristics of gold and its compounds have not been fully investigated. This is partly due to the fact that very few researches have been undertaken on the compounds of this metal, owing to its inaccessibility for working in large quantities. As the atomic weight of gold is high (Au = 197), the preparation of its compounds requires that it should be taken in large quantities, which forms an obstacle to its being fully studied. Hence the facts concerning the history of this metal are rarely distinguished by that exactitude with which many facts have been established concerning other elements more accessible, and long known in use.

crushing and washing.[29a] Nature has already accomplished a similar disintegration of the hard rocky matter containing gold.[30] These

---

[29a] Sonstadt (1872) showed that sea water, besides silver, always contains gold. Munster (1892) showed that the water of the Norwegian fiords contains about 5 milligrams of gold per ton (or 5 milliardths), i.e., a quantity deserving practical attention, and I think it may be already said that, considering the immense amount of sea water, in time means will be discovered for profitably extracting gold from sea water by bringing it into contact with substances capable of depositing gold upon their surface. The first efforts might be made upon the extraction of salt from sea water, and as the total amount of sea water may be taken as about 2,000,000,000,000,000,000 tons, it follows that it contains about 10,000 million tons of gold. The yearly production of gold is about 700 tons for the whole world. It is supposed that gold is dissolved in sea water owing to the presence of iodides, which, under the action of animal organisms, yield free iodine. It is thought, as Professor Konovaloff mentions, that iodine facilitates the solution of the gold, and the organic matter its precipitation. These facts and considerations explain to a certain extent the distribution of gold in veins or rock fissures, chiefly filled with quartz, because there is sufficient reason for supposing that these rocks once formed the ocean bottom. R. Dentrie, and subsequently Wilkinson, showed that organic matter—for instance, cork—and pyrites are able to precipitate gold from its solutions in that metallic form and state in which it occurs in quartz veins, where (especially in the deeper parts of vein deposits) gold is frequently found on the surface of pyrites, chiefly arsenical pyrites. Kazantseff (in Ekaterinburg, 1891) even supposes, from the distribution of the gold in these pyrites, that it occurred in solution as a compound of sulphide of gold and sulphide of arsenic when it penetrated into the veins. It is from such considerations that the origin of vein and pyritic gold is, at the present time, attributed to the reaction of solutions of this metal, the remains of which are seen in the gold still present in sea water.

[30] However, in recent times, especially since about 1870, when chlorine (either as a solution of the gas or as bleaching powder) and bromine began to be applied to the extraction of finely divided gold from poor ores (previously roasted in order to drive off arsenic and sulphur and oxidise the iron), the extraction of gold from quartz and pyrites by the wet method, increases from year to year, and begins to equal the amount extracted from alluvial deposits. Since the nineties the *cyanide process* (Chap. XIII., note 12) has taken an important place among the wet methods for extracting gold from its ores. It consists in pouring a dilute solution of cyanide of potassium (about 500 parts of water and 1 to 4 parts of cyanide of potassium per 1,000 parts of ore, the amount of cyanide depending upon the richness of the ore) and a mixture of it with NaCN, over the crushed ore (which need not be roasted, whilst roasting is indispensable in the chlorination process, as otherwise the chlorine is used up in oxidising the sulphur, arsenic, &c.). The gold is dissolved very rapidly even from pyrites, where it generally occurs on the surface in such fine and adherent particles that it either cannot be mechanically washed away, or, more frequently, is carried away by the stream of water, and cannot be caught by mechanical means or by the mercury used for catching the gold in the sluices. Chlorination had already given the possibility of extracting the finest particles of gold; but the cyanide process enables such pyrites to be treated as could scarcely be worked by other means. The treatment of the crushed ore by the KCN is carried on in simple wooden vats (coated with paraffin or tar) with the greatest possible rapidity (in order that the KCN solution should not have time to change) by a method of systematic lixiviation, and is completed in 10 to 12 hours. The participation of the oxygen of the air is indispensable for the reaction (Chap. XIII., note 13a) for: $2Au + 4KCN + O + H_2O = 2(KAuC_2N_2) + 2KHO$. The resultant solution of gold, containing $AuK(CN)_2$, is decomposed either with freshly made zinc filings (but when the gold settles on the Zn, the cyanide solution reacts upon the Zn with evolution of H_2 and formation of ZnH_2O_2) or by sodium amalgam prepared at the moment of reaction by the action of an electric current upon a solution of NaHO poured into a vessel partially immersed in mercury (the NaCN is

disintegrated rocks, washed by rain and other water, have formed gold-bearing deposits, which are known as **alluvial gold deposits.** Gold-bearing soil is sometimes met with on the surface and sometimes under the upper soil, but more frequently along the banks of dried-up water-courses and running streams. The sand of many rivers contains, however, a very small amount of gold, which it is not profitable to work; for example, that of the Alpine rivers contains 5 parts of gold in 10,000,000 parts of sand. The richest gold deposits are those of Siberia, especially in the southern parts of the government of Yeniseisk, the South Urals, Alaska, Mexico, California, South Africa, and Australia, and then come the comparatively poorer alluvial deposits of many countries (Hungary, the Alps, and Spain, in Europe). The extraction of the gold from alluvial deposits is based on the principle of levigation: the earth is washed, while constantly agitated, by a stream of water, which carries away the lighter portion of the earth, and leaves the coarser particles of the rock and heavier particles of the gold, together with certain substances which accompany it, in the washing apparatus. The extraction of this **washed** gold only necessitates mechanical appliances,[31] and it is not therefore surprising that gold was known to

---

continually renewed by this means). The silver in the ore passes into solution, together with the gold, as in amalgamation.

[31] But the particles of gold are sometimes so small that a large amount is lost during the washing. It is then profitable to have recourse to the extraction by chlorine and KCN (note 30). In speaking of the extraction of gold the following remarks may not be out of place: In California advantage is taken of water supplied from high altitudes in order to have a powerful head of water, with which the rocks are directly washed away, thus avoiding the greater portion of the mechanical labour required for the exploitation of these deposits. The last residues of gold are sometimes extracted from sand by washing them with mercury, which dissolves the gold. The sand mixed with water is caused to come into contact with mercury during the washing. The mercury is then distilled.

Many sulphurous ores, even pyrites, contain a small amount of gold. Compounds of gold with bismuth, $BiAu_2$, tellurium, $AuTe_2$ (calverite), &c., have been found, although rarely.

Among the minerals which accompany gold, and from which the presence of gold may be expected, we may mention white quartz, titanic and magnetic iron ores, and also the following, which are of rarer occurrence: zircon, topaz, garnet, and the like. The concentrated gold washings first undergo a mechanical treatment, and the impure gold obtained is treated for pure gold by various methods. If the gold contains a considerable amount of foreign metals, especially lead and copper, it is sometimes cupelled, like silver, so that the oxidisable metals may be absorbed by the cupel in the form of oxides; but in every case the gold is obtained together with silver, because the latter metal also is not oxidised. Sometimes the gold is extracted by means of mercury, that is, by amalgamation (and the mercury subsequently driven off by distillation), or by smelting it with lead (which is afterwards removed by oxidation) and processes like those employed for the extraction of silver, because gold, like silver, does not oxidise, is dissolved by lead and mercury, and is non-volatile. If copper or any other metal contain gold and it be employed as an anode, pure copper will be deposited upon the cathode, while all the gold will remain at the anode as a slime. This method often amply repays the whole cost of the process, since it gives, besides the gold, a pure electrolytic copper.

savages and in the most remote periods of history. It sometimes occurs in crystals belonging to the regular system, but in the majority of cases in nuggets or grains of greater or less magnitude. It always contains silver (from very small quantities up to 30 per cent., when it is called 'electrum') and certain other metals, among which lead and rhodium are sometimes found. About 400 tons of gold are annually produced by the world, and about 40 tons by Russia.

The separation of the silver from gold is generally carried on with great precision, as the presence of silver in the gold does not increase its value for exchange, and it can be substituted by other less valuable metals, so that the extraction of the silver, as a precious metal, from its alloy with gold, is a profitable operation. This separation is conducted by different methods. Sometimes the argentiferous gold is melted in crucibles, together with a mixture of common salt and powdered bricks. The greater portion of the silver is thus converted into the chloride, which fuses and is absorbed by the slags, from which it may be extracted by the usual methods. The silver is also extracted from gold by treating it with boiling sulphuric acid, which does not act on the gold but dissolves the silver. But if the alloy does not contain a large proportion of silver it cannot be extracted by this method, or at all events the separation will be imperfect, and therefore a fresh amount of silver is added (by fusion) to the gold, in such quantity that the alloy contains twice as much silver as gold (quartation). The silver which is added is preferably such as contains gold, which is very frequently the case. The alloy thus formed is poured in a thin stream into water, by which means it is obtained in a granulated form; it is then boiled with strong sulphuric acid, three parts of acid being used to one part of alloy. The sulphuric acid extracts all the silver without acting on the gold. It is best, however, to pour off the first portion of the acid, which has dissolved the silver, and then treat the residue of still imperfectly pure gold with a fresh quantity of sulphuric acid. The gold is thus obtained in the form of powder, which is washed with water until it is quite free from silver. The silver is precipitated from the solution by means of copper, so that cupric sulphate and metallic silver are obtained. This process is carried out in many countries, as in Russia, at the Government mints.

Gold is generally used alloyed with copper; since pure gold, like pure silver, is very soft, and therefore soon worn away. In assaying or determining the amount of pure gold in such an alloy it is usual to add silver to the gold in order to make up an alloy containing three parts of silver to one of gold (this is known as quartation because the alloy contains $\frac{1}{4}$ of gold), the resultant alloy being treated with nitric acid. If the silver is not in excess over the gold, it is not all dissolved by the nitric acid, and this is the reason for the quartation. The amount of pure gold (assay) is determined by weighing the gold which remains after this treatment. Russian, French, and other gold coin, and also many gold articles, are composed of an alloy containing 90 per cent. of gold. English gold coin contains $\frac{11}{12}$ Au.

Pure gold may be obtained from gold alloys by dissolving in aqua regia, and then adding ferrous sulphate to the solution or heating it with a solution of oxalic acid. These deoxidising agents reduce the gold, but not the other metals. The chlorine combined with the gold then acts like free chlorine. The gold, thus reduced, is precipitated as an exceedingly fine brown powder.[31a] It is then washed with water, and fused with nitre or borax. Pure gold reflects a yellow light, and in the form of very thin sheets (gold-leaf), into which it can be hammered and rolled,[31b] it transmits a bluish-green light. The specific gravity of gold is about 19·5, that of gold coin being about 17·1. It fuses at 1090°—at a higher temperature than silver—and can be drawn into exceedingly fine wires or hammered into thin sheets. With its softness and ductility, gold is distinguished for its tenacity, and a gold wire two millimetres thick breaks only under a load of 68 kilograms. Gold vaporises even at a furnace heat, and imparts a greenish colour to a flame passing over it in a furnace. Gold alloys with copper almost without changing its volume.[32] In its chemical aspect, gold presents,

---

[31a] Schottländer (1893) obtained gold in a soluble colloidal form (the solution is violet) by the action of a mixture of solutions of cerium acetate and NaHO upon a solution of $AuCl_3$. The gold separates out from such a solution in exactly the same manner as Ag does from the solution of colloidal silver mentioned above. There always remains a certain amount of a higher oxide of cerium, CeO_2, in the solution, i.e., the gold is reduced by converting the cerium into a higher grade of oxidation. Besides which, Krüss and Hofmann showed that sulphide of gold, precipitated by the action of H_2S upon a solution of $AuKCy_2$ mixed with HCl, easily passes into a colloidal solution after being properly washed (like As_2S_3, CuS, &c., Chap. I., note 57).

[31b] Gold-leaf is used for gilding wood (leather, cardboard, and similar material, upon which it is glued by means of varnish, &c.), and is about 0·003 millimetre thick. It is obtained from thin sheets (weighing at first about $\frac{1}{4}$ grm. to a square inch), rolled between gold rollers, by gradually hammering them (in packets of a number at once) between sheets of moist (but not wet) parchment, and then, after cutting them into four pieces, between a specially prepared membrane, which, when at the right degree of moisture, does not tear or stick together under the blows of the hammer.

[32] The formation of the alloys Cu + Zn, Cu + Sn, Cu + Bi, Cu + Sb, Pb + Sb, Ag + Pb, Ag + Sn, Au + Zn, Au + Sn, &c., is accompanied by a contraction (and evolution of heat). The formation of the alloys Fe + Sb, Fe + Pb, Cu + Pb, Pb + Sn, Pb + Sb, Zn + Sb, Ag + Cu, Au + Cu, Au + Pb, takes place with a certain increase in volume. With regard to the alloys of gold, it may be mentioned that gold is only slightly dissolved by mercury (about 0·06 per cent., Dudley, 1890); the remaining portion forms a

as is already seen from its general characteristics given above, an example of the so-called noble metals, i.e., it is incapable of being oxidised at any temperature, and its oxide is decomposed when calcined. Only chlorine and bromine combine directly with it at the ordinary temperature, but many other metals and non-metals combine with it at a red heat—for example, sulphur, phosphorus, and arsenic. Mercury dissolves it with great ease. It dissolves in potassium cyanide in the presence of air; a mixture of sulphuric acid with nitric acid dissolves it with the aid of heat, although in small quantity. It is also soluble in aqua regia and in selenic acid. Sulphuric, hydrochloric, nitric, and hydrofluoric acids and the caustic alkalies do not act on gold, but a mixture of hydrochloric acid with such oxidising agents as evolve chlorine naturally dissolves it, like aqua regia.[32a]

As regards the compounds of gold, they belong, as was said above, to the types AuX_3 and AuX. **Auric chloride** or **gold trichloride,** $AuCl_3$, which is formed when gold is dissolved in aqua regia, belongs to the former and higher of these types. The solution of this substance in water has a yellow colour, and it may be obtained pure by evaporating the solution in aqua regia to dryness, but not to the point of decomposition. If the evaporation proceeds to the point of crystallisation, compound of gold chloride and hydrochloric acid, $AuHCl_4$, is obtained, like the allied compounds of platinum; but it easily parts with the acid and leaves auric chloride, which fuses into a red-brown liquid, and then solidifies to a crystalline mass. If dry chlorine is passed over powdered gold it forms a mixture of aurous and auric chlorides, but the aurous chloride is also partly decomposed by water into

---

granular alloy, whose composition has not been definitely determined. Aluminium (and silicon) also have the capacity of forming alloys with gold. The presence of a small amount of aluminium lowers the melting-point of gold considerably (Roberts-Austen, 1892); thus, the addition of 4 per cent. of aluminium lowers it by 14·28°, the addition of 10 per cent. of Al by 41·7°; the latter alloy is white. The alloy $AuAl_2$ has a characteristic purple colour, and its melting-point is 32·5° above that of gold, which shows it to be a definite compound of the two metals. The melting-points of alloys richer in Al gradually fall to 660°—that is, below that of aluminium (665°).

Heycock and Neville (1892), in studying the triple alloys of Au, Cd, and Sn, observed a tendency in the gold to give compounds with Cd, and by sealing a mixture of Au and Cd in a tube, from which the air had been exhausted, and heating it, they obtained a grey crystalline brittle definite alloy, AuCd.

[32a] Calderon (1892), at the request of some jewellers, investigated the cause of a peculiar alteration sometimes found on the surface of dead-gold articles, there appearing brownish and blackish spots, which widen and alter their form in course of time. He came to the conclusion that these spots are due to the appearance and development on the gold of peculiar micro-organisms (*Aspergillus niger* and *Micrococcus cimbareus*), spores of which were found in abundance on the cotton-wool in which the gold articles had been kept.

gold and auric chloride. Auric chloride crystallises from its solutions as $AuCl_3,2H_2O$, which easily loses water, and the dry chloride loses two-thirds of its chlorine at 185°, forming aurous chloride, whilst above 300° the latter chloride also loses its chlorine and leaves metallic gold. Auric chloride is the usual form in which gold occurs in solutions, and in which its salts are used in the arts and for chemical purposes. It is soluble in water, alcohol, and ether. Light has a reducing action on these solutions, and after a time metallic gold is deposited upon the sides of vessels containing the solution. Hydrogen when nascent, and even in a gaseous form, reduces gold from this solution to a metallic state. The reduction is more conveniently and usually effected by ferrous sulphate, and by the action of ferrous salts in general.[33]

If a solution of potassium hydroxide is added to a solution of auric chloride, a precipitate is first formed, which re-dissolves in an excess of the alkali. On being evaporated under the receiver of an air-pump, this solution yields yellow crystals, which present the same composition as the double salts $AuMCl_4$, with the substitution of the chlorine by oxygen—that is to say, **potassium aurate**, $AuKO_2$, is formed, in crystals containing $3H_2O$. The solution has a distinctly alkaline reaction. **Auric oxide**, Au_2O_3, separates when this alkaline solution is boiled with an excess of sulphuric acid. But it then still retains some alkali; however, it may be obtained in a pure state as a brown powder by dissolving in nitric acid and diluting with water. The brown powder decomposes below 250° into gold and oxygen. It is insoluble in water and in many acids, but it dissolves in alkalies, which shows the acid character of this oxide. A hydroxide, $Au(OH)_3$, may be obtained as a brown powder by adding magnesium oxide to a solution of auric chlo-

---

[33] Stannous chloride as a reducing agent also acts on auric chloride, and gives a red precipitate known as **purple of Cassius**. This substance, which probably contains a mixture or compound of aurous oxide and tin oxide, is used as a red pigment for china and glass. Oxalic acid, on heating, reduces metallic gold from its salts, and this property may be taken advantage of for separating it from its solutions. The oxidation which then takes place in the presence of water may be expressed by the following equation: $2AuCl_3 + 3C_2H_2O_4 = 2Au + 6HCl + 6CO_2$. Nearly all organic substances have a reducing action on gold, and solutions of gold leave a violet stain on the skin.

Auric chloride, like platinic chloride, is distinguished for its clearly developed property of forming double salts. These double salts, as a rule, belong to the type $AuMCl_4$. The compound of auric chloride with hydrochloric acid mentioned above evidently belongs to the same type. The compounds $2KAuCl_4,5H_2O$; $NaAuCl_4,2H_2O$; $AuNH_4Cl_4,H_2O$; $Mg(AuCl_4)_2,2H_2O$, and the like are easily crystallised in well-formed crystals. Wells, Wheeler, and Penfield (1892) obtained $RbAuCl_4$ (reddish-yellow) and $CsAuCl_4$ (golden-yellow), and corresponding bromides (dark-coloured). $AuBr_3$ is extremely like the chloride. Auric cyanide is easily obtained in the form of a double salt of potassium, $KAu(CN)_4$, by mixing saturated and hot solutions of potassium cyanide with auric chloride and then cooling.

ride and treating the resultant precipitate of magnesium aurate with nitric acid. This hydroxide loses water at 100°, and gives auric oxide.[34]

The starting-point of the compounds of the type AuX [35] is **gold monochloride** or **aurous chloride,** AuCl, which is formed, as mentioned above, by heating auric chloride at 185°. Aurous chloride forms a yellowish-white powder; this, when heated with water, is decomposed into metallic gold and auric chloride, which passes into solution: $3AuCl = AuCl_3 + 2Au$. This decomposition is accelerated by the action of light. Hence it is obvious that the compounds corresponding with aurous oxide are comparatively unstable. But this only refers to the simple compounds AuX; some of the complex compounds, on the contrary, form the most stable compounds of gold. Such, for example, is the cyanide of gold and potassium, $AuK(CN)_2$. It is formed, for instance, when finely divided gold dissolves in the presence of air in a solution of potassium cyanide: $4KCN + 2Au + H_2O + O = 2KAu(CN)_2 + 2KHO$ (this reaction also proceeds with solid pieces of gold, although very slowly). The same compound is formed in solution when many compounds of gold are mixed with potassium cyanide, because if a higher compound of gold is taken, it is reduced

---

[34] If ammonia is added to a solution of auric chloride, it forms a yellow precipitate of the so-called fulminating gold, which contains gold, chlorine, hydrogen, nitrogen, and oxygen, but its formula is not known with certainty. It is probably a sort of ammonio-metallic compound, $Au_2O_3,4NH_3$, or amide (like the mercury compound). This precipitate explodes at 140°, but when left in the presence of solutions containing ammonia it loses all its chlorine and becomes non-explosive. In this form the composition $Au_2O_3,2NH_3,H_2O$ is ascribed to it, but this is uncertain. Auric sulphide, Au_2S_3, is obtained by the action of hydrogen sulphide on a solution of auric chloride, and also directly by fusing sulphur with gold. It has an acid character, and therefore dissolves in sodium and ammonium sulphides.

[35] Many double salts of suboxide of gold belong to the type AuX—for instance, the cyanide corresponding to the type $AuKX_2$, like PtK_2X_4, with which we became acquainted in the last chapter. If auric chloride, $AuCl_3$, is mixed with a solution of sodium thiosulphate, the gold passes into a colourless solution, which deposits colourless crystals of a double thiosulphate of gold and sodium, which are easily soluble in water but are precipitated by alcohol. The composition of this salt is $Na_3Au(S_2O_3)_2,2H_2O$. The solution of this colourless and easily crystallisable salt has a sweet taste, and the gold is not separated from it by either ferrous sulphate or oxalic acid. This salt, which is known as **Fordos and Gelis' salt,** is used in medicine and photography. In general, aurous oxide exhibits a distinct inclination to the formation of similar double salts, as we saw also with PtX_2—for example, it forms similar salts with sulphurous acid. Thus, if a solution of sodium sulphite is gradually added to a solution of oxide of gold in sodium hydroxide, the precipitate at first formed re-dissolves to a colourless solution, which contains the double salt $Na_3Au(SO_3)_2 = AuNa(SO_3Na)_2$. The solution of this salt when mixed with barium chloride, forms first a precipitate of barium sulphite, and then a red barium double salt which corresponds with the above sodium salt.

The oxygen compound of the type AuX, **aurous oxide,** Au_2O, is obtained as a greenish-violet powder on mixing aurous chloride with potassium chloride in the cold. With hydrochloric acid this oxide gives gold and auric chloride, and when heated it easily splits up into oxygen and metallic gold.

by the potassium cyanide to aurous oxide, which dissolves in potassium cyanide and forms $KAu(CN)_2$. This substance is soluble in water, and gives a colourless solution, which can be kept for a long time, and is employed in electro-gilding—that is, for coating other metallic objects with a layer of gold, which is deposited if the object is connected with the cathode, and the anode consists of a gold plate, and an electric current is passed between them.

(The original Russian Edition was put into the press in July 1902, and finished in January 1903.)

APPENDIX I

AN ATTEMPT TO APPLY TO CHEMISTRY ONE OF THE PRINCIPLES OF NEWTON'S NATURAL PHILOSOPHY

BY PROFESSOR MENDELÉEFF

A LECTURE DELIVERED AT THE ROYAL INSTITUTION OF GREAT BRITAIN
ON FRIDAY, MAY 31, 1889

NATURE, inert to the eyes of the ancients, has been revealed to us as full of life and activity. The conviction that motion pervaded all things, which was first realised with respect to the stellar universe, has now extended to the unseen world of atoms. No sooner had the human understanding denied to the earth a fixed position and launched it along its path in space, than it was sought to fix immovably the sun and the stars. But astronomy has demonstrated that the sun moves with unswerving regularity through the star-set universe at the rate of about 50 kilometres per second. Among the so-called fixed stars are now discerned manifold changes and various orders of movement. Light, heat, electricity—like sound—have been proved to be modes of motion; to the realisation of this fact modern science is indebted for powers which have been used with such brilliant success, and which have been expounded so clearly at this lecture table by Faraday and by his successors. As, in the imagination of Dante, the invisible air became peopled with spiritual beings, so before the eyes of earnest investigators, and especially before those of Clerk Maxwell, the invisible mass of gases became peopled with particles: their rapid movements, their collisions, and impacts became so manifest that it seemed almost possible to count the impacts and determine many of the peculiarities or laws of their collisions. The fact of the existence of these invisible motions may at once be made apparent by demonstrating the difference in the rate of diffusion through porous bodies of the light and rapidly moving atoms of hydrogen and the heavier and more sluggish particles of air. Within the masses of liquid and of solid bodies we have been forced to acknowledge the existence of persistent though limited motion of their ultimate particles, for otherwise it would be impossible to explain, for example, the celebrated experiments of Graham on diffusion through liquid and colloidal substances. If there were, in our times, no belief in the molecular motion in solid bodies, could the famous Spring have hoped to attain any result by mixing carefully dried powders of potash, saltpetre, and sodium acetate, in order to produce, by pressure, a chemical reaction between these substances through the interchange of their metals, and have derived, for the conviction of the incredulous, a mixture of two hygroscopic though solid salts—sodium nitrate and potassium acetate ?

In these invisible and apparently chaotic movements, reaching from the stars to the minutest atoms, there reigns, however, an harmonious order which is commonly mistaken for complete rest, but which is really a consequence of the conservation of that dynamic equilibrium which was first discerned by the genius of Newton, and which has been traced by his successors in the detailed analysis of the particular consequences of the great generalisation, namely, relative immovability in the midst of universal and active movement.

But the unseen world of chemical changes is closely analogous to the visible world of the heavenly bodies, since our atoms form distinct portions of an invisible world, as planets, satellites, and comets form distinct portions of the astronomer's universe; our atoms may therefore be compared to the solar systems, or to the systems of double or of single stars: for example, ammonia (NH_3) may be represented in the simplest manner by supposing the sun, nitrogen, surrounded by its planets of hydrogen; and common salt ($NaCl$) may be looked on as a double star formed of sodium and chlorine. Besides, now that the indestructibility of the elements has been acknowledged, chemical changes cannot otherwise be explained than as changes of motion, and the production by chemical reactions of galvanic currents, of light, of heat, of pressure, or of steam power, demonstrates visibly that the processes of chemical reaction are inevitably connected with enormous though unseen displacements, originating in the movements of atoms in molecules. Astronomers and natural philosophers, in studying the visible motions of the heavenly bodies and of matter on the earth, have understood and have estimated the value of this store of energy. But the chemist has had to pursue a contrary course. Observing in the physical and mechanical phenomena which accompany chemical reactions the quantity of energy manifested by the atoms and molecules, he is constrained to acknowledge that within the molecules there exist atoms in motion, endowed with an energy which, like matter itself, is neither being created nor capable of being destroyed. Therefore, in chemistry, we must seek dynamic equilibrium not only between the molecules, but also in their midst among their component atoms. Many conditions of such equilibrium have been determined, but much remains to be done, and it is not uncommon, even in these days, to find that some chemists forget that there is the possibility of motion in the interior of molecules, and therefore represent them as being in a condition of deathlike inactivity.

Chemical combinations take place with so much ease and rapidity, possess so many special characteristics, and are so numerous, that their simplicity and order were for a long time hidden from investigators. Sympathy, relationship, all the caprices or all the fancifulness of human intercourse, seemed to have found complete analogies in chemical combinations, but with this difference, that the characteristics of the material substances—such as silver, for example, or of any other body—remain unchanged in every subdivision from the largest masses to the smallest particles, and consequently these characteristics must be properties of the particles. But the world of heavenly luminaries appeared equally fanciful at man's first acquaintance with it, so much so, that the astrologers imagined a connection between the individualities of men and the conjunctions of planets. Thanks to the genius of Lavoisier and of Dalton, man has been able, in the unseen world of chemical combinations, to recognise laws of the same simple order as those which Copernicus and Kepler proved to exist in the planetary universe. Man discovered, and continues every hour to discover, *what* remains unchanged in chemical evolution, and *how* changes take place in combinations of the unchangeable. He has learned to predict, not only what possible combinations may take place, but also the very existence of atoms of unknown elementary substances, and has besides succeeded in making innumerable practical applications of his knowledge to the great advantage of his race, and has accomplished this notwithstanding that notions of sympathy and affinity still preserve a strong vitality in science. At present we cannot apply Newton's principles to chemistry, because the soil is only now being prepared. The invisible world of chemical atoms is still waiting for the creator of chemical mechanics. For him our age is collecting a mass of materials, the inductions of well-digested facts, and many-sided inferences similar to those which existed for Astronomy and Mechanics in the days of Newton. It is well also to remember that Newton devoted much time to chemical experiments, and, while considering questions of celestial mechanics, persistently kept in view the mutual action of those infinitely small worlds which are concerned in chemical evolutions. For this reason, and also to maintain the unity of laws, it seems to me that we must, in the first instance, seek to harmonise the various phases of contemporary chemical theories with the immortal principles of the Newtonian natural philosophy, and so hasten the advent of true chemical mechanics. Let the above considerations serve as my justification for the attempt which I propose to make to act as a champion of the universality of the Newtonian principles, which I believe are competent to embrace every phenomenon in the universe, from the rotation of the fixed stars to the interchanges of chemical atoms.

In the first place I consider it indispensable to bear in mind that, up to quite recent times, only a one-sided affinity has been recognised in chemical reactions. Thus, for example, from the circumstance that red-hot iron decomposes water with the evolution of hydrogen, it was concluded that oxygen had a greater affinity for iron than for hydrogen. But hydrogen, in presence of red-hot iron scale, appropriates its oxygen and forms water, whence an exactly opposite conclusion may be formed.

During the last ten years a gradual, scarcely perceptible, but most important change has taken place in the views, and consequently in the researches, of chemists. They have sought everywhere, and have always found, systems of conservation or dynamic equilibrium substantially similar to those which natural philosophers have long since discovered in the visible world, and in virtue of which the position of the heavenly bodies in the universe is determined. There where one-sided affinities only were at first detected, not only secondary or lateral ones have been found, but even those which are diametrically opposite ; yet among these, dynamical equilibrium establishes itself not by excluding one or other of the forces, but by regulating them all. So the chemist finds in the flame of the blast furnace, in the formation of every salt, and, with especial clearness, in double salts and in the crystallisation of solutions, not a fight ending in the victory of one side, as used to be supposed, but the conjunction of forces ; the peace of dynamic equilibrium resulting from the action of many forces and affinities. Carbonaceous matters, for example, burn at the expense of the oxygen of the air, yielding a quantity of heat, and forming products of combustion, in which it was thought that the affinities of the oxygen with the combustible elements were satisfied. But it appeared that the heat of combustion was competent to decompose these products, to dissociate the oxygen from the combustible elements, and therefore to explain combustion fully it is necessary to take into account the equilibrium between opposite reactions, between those which evolve and those which absorb heat.

In the same way, in the case of the solution of common salt in water, it is necessary to take into account, on the one hand, the formation of compound particles generated by the combination of salt with water, and, on the other, the disintegration or scattering of the new particles formed, as well as of these originally contained. At present we find two currents of thought, apparently antagonistic to each other, dominating the study of solutions: according to the one, solution seems a mere act of building up or association ; according to the other, it is only dissociation or disintegration. The truth lies, evidently, between these views ; it lies, as I have endeavoured to prove by my investigations into aqueous solutions, in the dynamic equilibrium of particles tending to combine and also to fall asunder. The large majority of chemical reactions which appeared to act victoriously along one line have been proved capable of acting as victoriously even along an exactly opposite line. Elements which utterly decline to combine directly may often be formed into comparatively stable compounds by indirect means, as, for example, in the case of chlorine and carbon ; and consequently the sympathies and antipathies which it was thought to transfer from human relations to those of atoms should be laid aside until the mechanism of chemical relations is explained. Let us remember, however, that chlorine, which does not form with carbon the chloride of carbon, is strongly absorbed, or, as it were, dissolved, by carbon, which leads us to suspect incipient chemical action even in an external and purely surface contact, and involuntarily gives rise to conceptions of that unity of the forces of nature which has been so energetically insisted on by Sir William Grove and formulated in his famous paradox. Grove noticed that platinum, when fused in the oxyhydrogen flame, during which operation water is formed, when allowed to drop into water decomposes the latter and produces the explosive oxyhydrogen mixture. The explanation of this paradox, as of many others which arose during the period of chemical renaissance, has led, in our time, to the promulgation by Henri Sainte-Claire Deville of the conception of dissociation and of equilibrium, and has recalled the teaching of Berthollet, which, notwithstanding its brilliant confirmation by Heinrich Rose and Dr. Gladstone, had not, up to that period, been included in received chemical views.

Chemical equilibrium in general, and dissociation in particular, are now being so fully worked out in detail, and applied in such various ways, that I do not allude to them to develop, but only use them as examples by which to indicate the correctness of a tendency to regard chemical combinations from points of view differing from those expressed by the term hitherto appropriated to define chemical forces, namely, 'affinity.' Chemical equilibria, dissociation, the speed of chemical reactions, thermochemistry, spectroscopy, and, more than all, the determination of the influence of masses and the search for a connection between the properties and weights of atoms and molecules—in one word, the vast mass of the most important chemical researches of the present day—clearly indicate the near approach of the time when chemical doctrines will submit fully and completely to the doctrine which was first announced in the 'Principia' of Newton.

In order that the application of these principles may bear fruit it is evidently insufficient to assume that statical equilibrium reigns alone in chemical systems or chemical molecules: it is necessary to grasp the conditions of possible states of dynamical equilibria, and to apply to them kinetic principles. Numerous considerations compel us to renounce the idea of statical equilibrium in molecules, and the recent yet strongly supported appeals to dynamic principles constitute, in my opinion, the foundation of the modern teaching relating to atomicity, or the valency of the elements, which usually forms the basis of investigations into organic or carbon compounds.

This teaching has led to brilliant explanations of very many chemical relations and to cases of isomerism, or the difference in the properties of substances having the same composition. It has been so fruitful in its many applications and in the foreshadowing of remote consequences, especially respecting carbon compounds, that it is impossible to deny its claims to be ranked as a great achievement of chemical science. Its practical application to the synthesis of many substances of the most complicated composition entering into the structure of organised bodies, and to the creation of an unlimited number of carbon compounds, among which the colours derived from coal tar stand prominently forward, surpass the synthetical powers of Nature itself. Yet this teaching, as applied to the structure of carbon compounds, is not on the face of it directly applicable to the investigation of other elements, because in examining the first it is possible to assume that the atoms of carbon have always a definite and equal number of affinities, whilst in the combinations of other elements this is evidently inadmissible. Thus, for example, an atom of carbon yields only one compound with four atoms of hydrogen and one with four atoms of chlorine in the molecule, whilst the atoms of chlorine and hydrogen unite only in the proportions of one to one. Simplicity is here evident, and forms a point of departure from which it is easy to move forward with firm and secure tread. Other elements are of a different nature. Phosphorus unites with three and with five atoms of chlorine, and consequently the simplicity and sharpness of the application of structural conceptions are lost. Sulphur unites only with two atoms of hydrogen, but with oxygen it enters into higher orders of combination. The periodic relationship which exists among all the properties of the elements—such, for example, as their ability to enter into various combinations—and their atomic weights, indicate that this variation in atomicity is subject to one perfectly exact and general law, and it is only carbon and its near analogues which constitute cases of permanently preserved atomicity. It is impossible to recognise, as constant and fundamental properties of atoms, powers which, in substance, have proved to be variable. But by abandoning the idea of permanence, and of the constant saturation of affinities—that is to say, by acknowledging the possibility of free affinities—many retain a comprehension of the atomicity of the elements 'under given conditions'; and on this frail foundation they build up structures composed of chemical molecules, evidently only because the conception of manifold affinities gives, at once, a simple statical method of estimating the composition of the most complicated molecules.

I shall enter neither into details, nor into the various consequences following from these views, nor into the disputes which have sprung up respecting them (and relating especially to the number of isomerides possible on the assumption of free affinities), because the foundation or origin of theories of this nature suffers from the radical defect of being in opposition to dynamics. The molecule, as even Laurent expressed himself, is represented as an architectural structure, the style of which is determined by the fundamental arrangement of a few atoms, whilst the decorative details, which are capable of being varied by the same forces, are formed by the elements entering into the combination. It is on this account that the term 'structural' is so appropriate to the contemporary views of the above order, and that the 'structuralists' seek to justify the tetrahedral, plane, or prismatic disposition of the atoms of carbon in benzene. It is evident that the consideration relates to the statical position of atoms and molecules and not to their kinetic relations. The atoms of the structural type are like the lifeless pieces on a chessboard: they are endowed but with the voices of living beings, and are not those living beings themselves; acting, indeed, according to laws, yet each possessed of a store of energy which, in the present state of our knowledge, must be taken into account.

In the days of Haüy, crystals were considered in the same statical and structural light, but modern crystallographers, having become more thoroughly acquainted with their physical properties and their actual formation, have abandoned the earlier views, and have made their doctrines dependent on dynamics.

The immediate object of this lecture is to show that, starting with Newton's third law of motion, it is possible to preserve to chemistry all the advantages arising from structural teaching, without being obliged to build up molecules in solid and motionless figures, or to ascribe to atoms definite limited valencies, directions of cohesion, or affinities. The wide extent of the subject obliges me to treat of only a small portion of it, namely, of *substitutions*, without specially considering combinations and decompositions, and even then limiting myself to the simplest examples, which, however, will throw open prospects embracing all the natural complexity of chemical relations. For this reason, if it should prove possible to form groups similar, for example, to H_4 or CH_6 as the remnants of molecules CH_4 or C_2H_7 we shall not pause to consider them, because, as far as we know, they fall asunder into two parts, $H_2 + H_2$ or $CH_4 + H_2$, as soon as they are even temporarily formed, and are incapable of separate existence, and therefore can take no part in the elementary act of substitution. With respect to the simplest molecules which we shall select—that is to say, those of which the parts have no separate existence, and therefore cannot appear in substitutions—we shall consider them according to the periodic law, arranging them in direct dependence on the atomic weight of the elements.

Thus, for example, the molecules of the simplest hydrogen compounds—

HF	H_2O	H_3N	H_4C
hydrofluoric acid	water	ammonia	methane

correspond with elements the atomic weights of which decrease consecutively

$$F = 19, \quad O = 16, \quad N = 14, \quad C = 12.$$

Neither the arithmetical order (1, 2, 3, 4 atoms of hydrogen) nor the total information we possess respecting the elements will permit us to interpolate into this typical series one more additional element; and therefore we have here, for hydrogen compounds, a natural base on which are built up those simple chemical combinations which we take as typical. But even they are competent to unite with each other, as we see, for instance, in the property which hydrofluoric acid has of forming a hydrate—that is, of combining with water; and a similar attribute of ammonia, resulting in the formation of a caustic alkali, NH_3,H_2O, or NH_4OH.

Having made these indispensable preliminary observations, I may now attack the problem itself and attempt to explain the so-called structure, or rather construction, of molecules—that is to say, their constitution and transformations—without having recourse to the teaching of 'structuralists,' but on Newton's dynamical principles.

Of Newton's three laws of motion, only the third can be applied directly to chemical molecules when regarded as systems of atoms among which it must be supposed that there exist common influences or forces, and resulting compounded relative motions. Chemical reactions of every kind are undoubtedly accomplished by changes in these internal movements, respecting the nature of which nothing is known at present, but the existence of which the mass of evidence collected in modern times forces us to acknowledge as forming part of the common motion of the universe, and as a fact further established by the circumstance that chemical reactions are always characterised by changes of volume or the relations between the atoms or the molecules. Newton's third law, which is applicable to every system, declares that 'action is also associated with reaction, and is equal to it.' The brevity or conciseness of this axiom was, however, qualified by Newton in a more expanded statement, 'the actions of bodies one upon another are always equal, and in opposite directions.' This simple fact constitutes the point of departure for explaining dynamic equilibrium—that is to say, systems of conservancy. It is capable of satisfying even the dualists, and of explaining, without additional assumptions, the preservation of those chemical types which Dumas, Laurent, and Gerhardt created unit types, and those views of atomic combinations which the structuralists express by atomicity or the valency of the elements, and, in connection with them, the various numbers of affinities. In reality, if a system of atoms or a molecule be given, then in it, according to the third law of Newton, each portion of atoms acts on the remaining portion in the same manner, and with the same force as the second set of atoms acts on the first. We infer directly from this consideration that both sets of atoms, forming a molecule, are not only equivalent with regard to themselves, as they must be according to Dalton's law, but also that they may, if united, replace each other. Let there be a molecule containing atoms A B C, it is clear that, according to Newton's law, the action of A on B C must be equal to the action of B C on A, and if the first action is directed on B C, then the second must be directed on A, and consequently then, where A can exist in dynamic equilibrium, B C may take its place and act in a like manner. In the same way the action of C is equal to the action of A B. In one word every two sets of atoms forming a molecule are equivalent to each other, and may take each other's place in other molecules, or, having the power of balancing each other, the atoms or their complements are endowed with the power of replacing each other. Let us call this consequence of an evident axiom 'the principle of substitution,' and let us apply it to those typical forms of hydrogen compounds which we have already discussed, and which, on account of their simplicity and regularity, have served as starting-points of chemical argument long before the appearance of the doctrine of structure.

In the type of hydrofluoric acid, HF, or in systems of double stars, are included a multitude of the simplest molecules. It will be sufficient for our purpose to recall a few: for example, the molecules of chlorine, Cl_2, and of hydrogen, H_2, and hydrochloric acid, HCl, which is familiar to all in aqueous solution as spirits of salt, and which has many points of resemblance with HF, HBr, HI. In these cases division into two parts can only be made in one way, and therefore the principle of substitution renders it probable that exchanges between the chlorine and the hydrogen can take place, if they are competent to unite with each other. There was a time when no chemist would even admit the idea of any such action; it was then thought that the power of combination indicated a polar difference of the molecules in combination, and this thought set aside all idea of the substitution of one component element by another.

Thanks to the observations and experiments of Dumas and Laurent fifty years ago, such fallacies were dispelled, and in this manner the principle of substitution was exhibited. Chlorine and bromine, acting on many hydrogen compounds, occupy immediately the place of their hydrogen, and the displaced hydrogen, with another atom of chlorine or bromine, forms hydrochloric acid or bromide of hydrogen. This takes place in all typical hydrogen compounds. Thus chlorine acts on this principle on gaseous hydrogen—reaction, under the influence of light, resulting in the formation of hydrochloric acid. Chlorine acting on the alkalies, constituted similarly to water, and even on water itself--only, however, under the influence of light and only partially because of the instability of HClO—forms by this principle bleaching salts, which are the same as the alkalies, but with their hydrogen replaced by chlorine. In ammonia and in methane, chlorine can also replace the hydrogen. From ammonia is formed in this manner the so-called chloride of nitrogen, NCl_3, which decomposes very readily with violent explosion on account of the evolved gases, and falls asunder as chlorine and nitrogen. Out of marsh gas, or methane, CH_4, may be obtained consecutively, by this method, every possible substitution, of which chloroform, $CHCl_3$, is the best known, and carbon tetrachloride, CCl_4, the most instructive. But by virtue of the fact that chlorine and bromine act, in the manner shown, on the simplest typical hydrogen compounds, their action on the more complicated ones may be assumed to be the same. This can be easily demonstrated. The hydrogen of benzene, C_6H_6, reacts feebly under the influence of light on liquid bromine, but Gustavson has shown that the addition of the smallest quantity of metallic aluminium causes energetic action and the evolution of large volumes of hydrogen bromide.

If we pass on to the second typical hydrogen compound—that is to say, water—its molecule, HOH, may be split up in two ways: either into an atom of hydrogen and a semi-molecule of hydrogen peroxide, HO, or into oxygen, O, and two atoms of hydrogen, H; and therefore, according to the principle of substitution, it is evident that one atom of hydrogen can exchange with hydrogen oxide, HO, and two atoms of hydrogen, H, with one atom of oxygen, O.

Both these forms of substitution will constitute methods of oxidation—that is to say, of the entrance of oxygen into the compound—a reaction which is so common in nature as well as in the arts, taking place at the expense of the oxygen of the air or by the aid of various oxidising substances or bodies which part easily with their oxygen. There is no occasion to reckon up the unlimited number of cases of such oxidising reactions. It is sufficient to state that in the first of these oxygen is directly transferred, and the position, the chemical function, which hydrogen originally occupied, is, after the substitution, occupied by the hydroxyl. Thus ammonia, NH_3, yields hydroxylamine, $NH_2(OH)$, a substance which retains many of the properties of ammonia.

Methane and a number of other hydrocarbons yield, by substitution of the hydrogen by its oxide, methyl alcohol, $CH_3(OH)$, and other alcohols. The substitution of one atom of oxygen for two atoms of hydrogen is equally common with hydrogen compounds. By this means alcoholic liquids containing ethyl alcohol, or spirits of wine, $C_2H_5(OH)$, are oxidised until they become vinegar, or acetic acid, $C_2H_3O(OH)$. In the same way caustic ammonia, or the combination of ammonia with water, NH_3H_2O, or $NH_4(OH)$, which contains a great deal of hydrogen, by oxidation exchanges four atoms of hydrogen for two atoms of oxygen, and becomes converted into nitric acid, $NO_2(OH)$. This process of conversion of ammonium salts into saltpetre goes on in the fields every summer, and with especial rapidity in tropical countries. The method by which this is accomplished, though complex, though involving the agency of all-permeating micro-organisms, is, in substance, the same as that by which alcohol is converted into acetic acid, or glycol, $C_2H_4(OH)_2$, into oxalic acid, if we view the process of oxidation in the light of the Newtonian principles.

But while speaking of the application of the principle of substitution to water, we need not multiply instances, but must turn our attention to two special circumstances which are closely connected with the very mechanism of substitutions.

In the first place, the replacement of two atoms of hydrogen by one atom of oxygen may take place in two ways, because the hydrogen molecule is composed of two atoms, and therefore, under the influence of oxygen, the molecule forming water may separate before the oxygen has time to take its place. It is for this reason that we find, during the conversion of alcohol into acetic acid, that there is an interval during which is formed aldehyde, C_2H_4O, which, as its very name implies, is 'alcohol dehydrogenatum,' or alcohol deprived of hydrogen. Hence aldehyde combined with hydrogen yields alcohol; and united to oxygen, acetic acid.

For the same reason there should be, and there actually are, intermediate products between ammonia and nitric acid, $NO_2(HO)$, containing either less hydrogen than ammonia, less oxygen than nitric acid, or less water than caustic ammonia. Accordingly we find, among the products of the deoxidation of nitric acid and the oxidation of ammonia, not only hydroxylamine, but also nitrous oxide, nitrous and nitric anhydrides. Thus, the production of nitrous acid results from the removal of two atoms of hydrogen from caustic ammonia and the substitution of the oxygen for the hydrogen, $NO(OH)$; or by the substitution, in ammonia, of three atoms of hydrogen by hydroxyl, $N(OH)_3$, and by the removal of water: $N(OH)_3 - H_2O = NO(OH)$. The peculiarities and properties of nitrous acid—as, for instance, its action on ammonia and its conversion, by oxidation, into nitric acid—are thus clearly revealed.

On the other hand, in speaking of the principle of substitution as applied to water, it is necessary to observe that hydrogen and hydroxyl, H and OH, are not only competent to unite, but also to form combinations with themselves, and thus become H_2 and H_2O_2; and such are hydrogen and the peroxide thereof. In general, if a molecule A B exists, then molecules A A and B B can exist also. A direct reaction of this kind does not, however, take place in water, therefore undoubtedly, at the moment of formation, hydrogen reacts on hydrogen peroxide, as we can show at once by experiment; and further because hydrogen peroxide, H_2O_2, exhibits a structure containing a molecule of hydrogen, H_2, and one of oxygen, O_2, either of which is capable of separate existence. The fact, however, may now be taken as thoroughly established, that, at the moment of combustion of hydrogen or of the hydrogen compounds, hydrogen peroxide is always formed, and not only so, but in all probability its formation invariably precedes the formation of water. This was to be expected as a consequence of the law of Avogadro and Gerhardt, which leads us to expect this sequence in the case of equal interactions of volumes of vapours and gases; and in hydrogen peroxide we actually have such equal volumes of the elementary gases.

The instability of hydrogen peroxide—that is to say, the ease with which it decomposes into water and oxygen, even at the mere contact of porous substances—accounts for the circumstance that it does not form a permanent product of combustion, and is not produced during the decompostion of water. I may mention this additional consideration that, with respect to hydrogen peroxide, we may look for its effecting still further substitutions of hydrogen by means of which we may expect to obtain still more highly oxidised water compounds, such as H_2O_3 and H_2O_4. These Schönbein and Bunsen have long been seeking, and Berthelot is investigating them at present. It is probable, however, that the reaction will stop at the last compound, because we find that, in a number of cases, the addition of four atoms of oxygen seems to form a limit. Thus, OsO_4, $KClO_4$, $KMnO_4$, K_2SO_4, Na_3PO_4, and such like, represent the highest grades of oxidation.[1]

As for the last forty years, from the times of Berzelius, Dumas, Liebig, Gerhardt, Williamson, Frankland, Kolbe, Kekulé, and Butleroff, most theoretical generalisations have centred round organic or carbon compounds, we will, for the sake of brevity, leave out the discussion of ammonia derivatives, notwithstanding their simplicity with respect to the doctrine of substitutions; we will dwell more especially on its application to carbon compounds, starting from methane, CH_4, as the simplest of the hydrocarbons, containing in its molecule one atom of carbon. According to the principles enumerated we may derive from CH_4 every combination of the form CH_3X, CH_2X_2, CHX_3, and CX_4, in which X is an element, or radicle, equivalent to hydrogen—that is to say, competent to take its place or to combine with it. Such are the chlorine substitutes already mentioned, such is wood-spirit, $CH_3(OH)$, in which X is represented by the residue of water, and such are numerous other carbon derivatives. If we continue, with the aid of hydroxyl, further substitutions of the hydrogen of methane, we shall obtain successively $CH_2(OH)_2$, $CH(OH)_3$, and $C(OH)_4$. But if, in proceeding thus, we bear in mind that $CH_2(OH)_2$ contains two hydroxyls in the same form as hydrogen peroxide, H_2O_2 or $(OH)_2$, contains them—and moreover not only in one molecule, but together, attached to one and the same atom of carbon—so here we must look for the same decomposition as that which we find in hydrogen peroxide, and accompanied also by the formation of water as an independently existing molecule; therefore $CH_2(OH)_2$ should yield, as it actually does, immediately water and the oxide of methylene, CH_2O, which is methane with

---

[1] Because more than four atoms of hydrogen never unite with one atom of the elements, and because the hydrogen compounds (e.g., HCl, H_2S, H_3P, H_4Si) always form their highest oxides with four atoms of oxygen, and as the highest forms of oxides (OsO_4, RuO_4) also contain four of oxygen, and eight groups of the periodic system, corresponding to the highest basic oxides R_2O, RO, R_2O_3, RO_2, R_2O_5, RO_3, R_2O_7, and RO_4, imply the above relationship, and because of the nearest analogues among the elements—such as Mg, Zn, Cd, and Hg; or Cr, Mo, W, and U; or Si, Ge, Sn, and Pt; or F, Cl, Br, and I, and so forth—not more than four are known, it seems to me that in these relationships there lies a deep interest and meaning with regard to chemical mechanics. But because, to my imagination, the idea of unity of design in Nature, either acting in complex celestial systems or among chemical molecules, is very attractive, especially because the atomic teaching at once acquires its true meaning, I will recall the following facts relating to the solar system. There are eight major planets, of which the four inner ones are not only separated from the four outer by asteroids, but differ from them in many respects, as, for example, in the smallness of their diameters and their greater density. Saturn with his ring has eight satellites, Jupiter and Uranus have each four. It is evident that in the solar systems also we meet with these higher numbers four and eight which appear in the combination of chemical molecules.

oxygen substituted for two atoms of hydrogen. Exactly in the same manner, out of $CH(OH)_3$ are formed water and formic acid, $CHO(OH)$, and out of $C(OH)_4$ are produced water and carbonic acid, or directly carbonic anhydride, CO_2, which will therefore be nothing else than methane with the double replacement of pairs of hydrogen by oxygen. As nothing leads to the supposition that the four atoms of hydrogen in methane differ one from the other, so it does not matter by what means we obtain any one of the combinations indicated—they will be identical; that is to say, there will be no case of actual isomerism, although there may easily be such cases of isomerism as have been distinguished by the term metamerism.

Formic acid, for example, has two atoms of hydrogen, one attached to the carbon left from the methane, and the other attached to the oxygen which has entered in the form of hydroxyl, and if one of them be replaced by some substance X it is evident that we shall obtain substances of the same composition, but of different construction, or of different orders of movement among the molecules, and therefore endowed with other properties and reactions. If X be methyl, CH_3—that is to say, a group capable of replacing hydrogen because it is actually contained with hydrogen in methane itself—then by substituting this group for the original hydrogen we obtain acetic acid $CCH_3O(OH)$, out of formic, and by substitution of the hydrogen in its oxide or hydroxyl we obtain methyl formate, $CHO(OCH_3)$. These substances differ so much from each other physically and chemically that at first sight it is hardly possible to admit that they contain the same atoms in identically the same proportions. Acetic acid, for example, boils at a higher temperature than water, and has a higher specific gravity than it, whilst its metameride, methyl formate, is lighter than water, and boils at 30°—that is to say, it evaporates very easily.

Let us now turn to carbon compounds containing two atoms of carbon to the molecule, as in acetic acid, and proceed to evolve them from methane by the principle of substitution. This principle declares at once that methane can only be split up in the four following ways:—

1. Into a group CH_3 equivalent with H. Let us call changes of this nature methylation.
2. Into a group CH_2 and H_2. We will call this order of substitutions methylenation.
3. Into CH and H_3, which commutations we will call acetylenation.
4. Into C and H_4, which may be called carbonation.

It is evident that hydrocarbon compounds containing two atoms of carbon can only proceed from methane, CH_4, which contains four atoms of hydrogen by the first three methods of substitution; carbonation would yield free carbon if it could take place directly, and if the molecule of free carbon—which is in reality very complex, that is to say, strongly polyatomic, as I have long since been proving by various means—could contain only C_2 like the molecules O_2, H_2, N_2, and so on.

By methylation we should evidently obtain from marsh gas, ethane, $CH_3CH_3 = C_2H_6$.

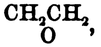
By methylenation—that is, by substituting group CH_2 for H_2—methane forms ethylene, $CH_2CH_2 = C_2H_4$.

By acetylenation—that is, by substituting three atoms of hydrogen, H_3, in methane—by the remnant CH, we get acetylene, $CHCH = C_2H_2$.

If we have applied the principles of Newton correctly, there should not be any other hydrocarbons containing two atoms of carbon in the molecule. All these combinations have long been known, and in each of them we can produce not only those substitutions of which an example has been given in the case of methane, but also all the phases of other substitutions, as we shall find from a few more instances, by the aid of which I trust that I shall be able to show the great complexity of those derivatives which, on the principle of substitution, can be obtained from each hydrocarbon. Let us content ourselves with the case of ethane, CH_3CH_3, and the substitution of the hydrogen by hydroxyl. The following are the possible changes :—

1. $CH_3CH_2(OH)$: this is nothing more than spirit of wine, or ethyl alcohol, $C_2H_5(OH)$ or C_2H_6O.

2. $CH_2(OH)CH_2(OH)$: this is the glycol of Würtz, which has shed so much light on the history of alcohol. Its isomeride may be $CH_3CH(OH)_2$, but as we have seen in the case of $OH(OH)_2$, it decomposes, giving off water, and forming aldehyde, CH_3CHO, a substance capable of yielding alcohol by uniting with hydrogen, and of yielding acetic acid by uniting with oxygen.

If glycol, $CH_2(OH)CH_2(OH)$, loses its water, it may be seen at once that it will not now yield aldehyde, CH_3CHO, but its isomeride,  $\underset{O}{CH_2CH_2}$, the oxide of ethylene. I have here indicated in a special manner the oxygen which has taken the place of two atoms of the hydrogen of ethane taken from different atoms of the carbon.

3. $CH_3C(OH)_3$ decomposed as $CH(OH)_3$, forming water and acetic acid, $CH_3CO(OH)$. It is evident that this acid is nothing else than formic acid, $CHO(OH)$, with its hydrogen replaced by methyl. Without examining further the vast number of possible derivatives, I will direct your attention to the circumstance that in dissolving acetic acid in water we obtain the maximum contraction with the greatest viscosity when to the molecule $CH_3CO(OH)$ is added a molecule of water, which is the proportion which would form the hydrate $CH_3C(OH)_3$. It is probable that the doubling of the molecule of acetic acid at temperatures approaching its boiling-point has some connection with this power of uniting with one molecule of water.

4. $CH_2(OH)C(OH)_3$ is evidently an alcoholic acid, and indeed this compound, after losing water, answers to glycolic acid, $CH_2(OH)CO(OH)$. Without investigating all the possible isomerides, we will note only that the hydrate $CH(OH)_2CH(OH)_2$ has the same composition as $CH_2(OH)C(OH)_3$, and although corresponding to glycol, and being a symmetrical substance, it becomes, on parting with its water, the aldehyde of oxalic acid, or the glyoxal of Debus, CHOCHO.

5. $CH(OH)_2C(OH_3)$, from the tendency of all the preceding, corresponds with glyoxylic acid, an aldehyde acid, CHCCO(OH), because the group CO(OH), or carboxyl, enters into the compositions of organic acids, and the group CHO defines the aldehyde function.

6. $C(OH)_3C(OH)_3$ through the loss of $2H_2O$ yields the bibasic oxalic acid

CO(OH)CO(OH), which generally crystallises with $2H_2O$, following thus the normal type of hydration characteristic of ethane.[2]

Thus, by applying the principle of substitution, we can, in the simplest manner, derive not only every kind of hydrocarbon compound, such as the alcohols, the aldehyde-alcohols, aldehydes, alcohol-acids, and the acids, but also combinations analogous to hydrated crystals which usually are disregarded.

But even those unsaturated substances, of which ethylene, CH_2CH_2, and acetylene, CHCH, are types, may be evolved with equal simplicity. With respect to the phenomena of isomerism, there are many possibilities among the hydrocarbon compounds containing two atoms of carbon, and without going into details it will be sufficient to indicate that the following formulæ, though not identical, will be isomeric substantially among themselves:—CH_3CHX_2 and CH_2XCH_2X, although both contain $C_2H_4X_2$; or CH_2CX_2 and CHXCHX, although both contain $C_2H_2X_2$, if by X we indicate chlorine or generally an element capable of replacing one atom of hydrogen, or capable of uniting with it. To isomerism of this kind belongs the case of aldehyde and the oxide of ethylene, to which we have already referred, because both have the composition C_2H_4O.

What I have said appears to me sufficient to show that the principle of substitution adequately explains the composition, the isomerism, and all the diversity of combination of the hydrocarbons, and I shall limit the further development of these views to preparing a complete list of every possible hydrocarbon compound containing three atoms of carbon in the molecule. There are eight in all, of which only five are known at present.[3]

Among those possible for C_3H_6 there should be two isomerides, propylene and trimethylene, and they are both already known. For C_3H_4 there should be three isomerides: allylene and allene are known, but the third has not yet been discovered; and for C_3H_2 there should be two isomerides, though neither of them is known as yet. Their composition and structure are easily

---

[2] One more isomeride, $CH_2CH(OH)$, is possible—that is, secondary vinyl alcohol, which is related to ethylene, CH_2CH_2, but derived by the principle of substitution from CH_4. Other isomerides, of the composition C_2H_4O, such, for example, as $CCH_3(OH)$, are impossible, because it would correspond with the hydrocarbon $CHCH_3 = C_2H_4$, which is isomeric with ethylene, and it cannot be derived from methane. If such an isomeride existed it would be derived from CH_2, but such products are, up to the present, unknown. In such cases the insufficiency of the points of departure of the statical structural teaching is shown. It first admits constant atomicity and then rejects it, the facts serving to establish either one or the other view; and therefore it seems to me that we must come to the conclusion that the structural method of reasoning, having done a service to science, has outlived the age, and must be regenerated, as in their time was the teaching of the electro-chemists, the radicalists, and the adherents of the doctrine of types. As we cannot now lean on the views above stated, it is time to abandon the structural theory. They will all be united in chemical mechanics, and the principle of substitution must be looked on only as a preparation for the coming epoch in chemistry, where such cases as the isomerism of fumaric and maleic acids, when explained dynamically, as proposed by Le Bel and van't Hoff, may yield points of departure.

[3] Conceding variable atomicity, the structuralists must expect an incomparably larger number of isomerides, and they cannot now decline to acknowledge the change of atomicity, were it only for the examples HgCl and $HgCl_2$, CO and CO_2, PCl_3 and PCl_5.

deduced from ethane, ethylene, and acetylene by methylation, by methylenation, by acetylination, and by carbonation.

1. $C_3H_8 = CH_3CH_2CH_3$ out of CH_3CH_3 by methylation. This hydrocarbon is named propane.

2. $C_3H_6 = CH_3CHCH_2$ out of CH_3CH_3 by methylenation. This substance is propylene.

3. $C_3H_6 = CH_2CH_2CH_2$ out of CH_3CH_3 by methylenation. This substance is trimethylene.

4. $C_3H_4 = CH_3CCH$ out of CH_3CH_3 by acetylenation or from CHCH by methylation. This hydrocarbon is named allylene.

5. $C_3H_4 = \begin{matrix}CHCH\\CH_2\end{matrix}$ out of CH_3CH_3 by acetylenation, or from CH_2CH_2 by methylenation, because $\begin{matrix}CH_2CH\\CH\end{matrix} = \begin{matrix}CHCH\\CH_2\end{matrix}$. This body is as yet unknown.

6. $C_3H_4 = CH_2CCH_2$ out of CH_2CH_2 by methylenation. This hydrocarbon is named allene, or iso-allylene.

7. $C_3H_2 = \begin{matrix}CHCH\\C\end{matrix}$ out of CH_3CH_3 by symmetrical carbonation, or out of CH_2CH_2 by acetylenation. This compound is unknown.

8. $C_3H_2 = \begin{matrix}CC\\CH_2\end{matrix}$ out of CH_3CH_3 by carbonation, or out of CHCH by methylenation. This compound is unknown.

If we bear in mind that for each hydrocarbon serving as a type in the above tables there are a number of corresponding derivatives, and that every compound obtained may, by further methylation, methylenation, acetylenation, and carbonation, produce new hydrocarbons, and these may be followed by a numerous suite of derivatives and an immense number of isomeric substances, it is possible to understand the limitless number of carbon compounds, although they all have the one substance, methane, for their origin. The number of substances is so enormous that it is no longer a question of enlarging the possibilities of discovery, but rather of finding some means of testing them analogous to the well-known two which for a long time have served as gauges for all carbon compounds.

I refer to the law of even numbers and to that of limits, the first enunciated by Gerhardt some forty years ago, with respect to hydrocarbons, namely, that their molecules always contain an even number of atoms of hydrogen. But by the method which I have used of deriving all the hydrocarbons from methane, CH_4, this law may be deduced as a direct consequence of the principle of substitutions. Accordingly, in methylation, CH_3 takes the place of H, and therefore CH_2 is added. In methylenation the number of atoms of hydrogen remains unchanged, and at each acetylenation it is reduced by two, and in carbonation by four, atoms—that is to say, an even number of atoms of hydrogen is always added or removed. And because the fundamental hydrocarbon, methane, CH_4, contains an even number of atoms of hydrogen, all its derivative hydrocarbons will also contain even numbers of hydrogen, and this constitutes the law of even numbers.

The principle of substitutions explains with equal simplicity the conception of the limiting compositions of hydrocarbons C_nH_{2n+2}, which I derived, in

1861,[4] in an empirical manner from accumulated materials available at that time, and on the basis of the limits to combinations worked out by Dr. Frankland for other elements.

Of all the various substitutions the highest proportion of hydrogen is yielded by methylation, because in that operation alone does the quantity of hydrogen increase; hence, taking methane as a point of departure, if we imagine methylation effected $(n-1)$ times we obtain hydrocarbon compounds containing the highest quantities of hydrogen. It is evident that they will contain $CH_4 + (n-1)CH_2$, or C_nH_{2n+2}, because methylation leads to the addition of CH_2 to the compound.

It will thus be seen that by the principle of substitution—that is to say, by the third law of Newton—we are able to deduce, in the simplest manner, not only the individual composition, the isomerism, and relations of substances, but also the general laws which govern their most complex combinations without having recourse either to statical constructions, to the definition of atomicities, to the exclusion of free affinities, or to the recognition of those single, double, or treble bonds which are so indispensable to structuralists in the explanation of the composition and construction of hydrocarbon compounds. And yet, by the application of the dynamical principles of Newton, we can attain to that chief and fundamental object, the comprehension of isomerism in hydrocarbon compounds, and the forecasting of the existence of combinations as yet unknown, by which the edifice raised by structural teaching is strengthened and supported. Besides—and I count this for a circumstance of special importance—the process which I advocate will make no difference in those special cases which have been already so well worked out, such as, for example, the isomerism of the hydrocarbons and alcohols, even to the extent of not interfering with the nomenclature which has been adopted, and the structural system will retain all the glory of having worked up, in a thoroughly scientific manner, the store of information which Gerhardt had accumulated about the middle of the fifties, and the still higher glory of establishing the rational synthesis of organic substances. Nothing will be lost to the structural doctrine except its statical origin; and as soon as it will embrace the dynamic principles of Newton, and suffer itself to be guided by them, I believe that we shall attain for chemistry that unity of principle which is now wanting. Many an adept will be attracted to that brilliant and fascinating enterprise, the penetration into the unseen world of the kinetic relations of atoms, to the study of which the last twenty-five years have contributed so much labour and such high inventive faculties.

D'Alembert found in mechanics that if inertia be taken to represent force, dynamic equations may be applied to statical questions, which are thereby rendered more simple and more easily understood.

The structural doctrine in chemistry has unconsciously followed the same course, and therefore its terms are easily adopted; they may retain their present forms provided that a truly dynamical—that is to say, Newtonian—meaning be ascribed to them.

Before finishing my task and demonstrating the possibility of adapting

---

[4] 'Essai d'une Théorie sur les Limites des Combinaisons organiques,' par D. Mendeléeff, 2/11 août 1861, *Bulletin de l'Académie i. d. Sc. de St-Pétersbourg*, tom. v.

structural doctrines to the dynamics of Newton, I consider it indispensable to touch on one question which naturally arises, and which I have heard discussed more than once. If bromine, the atom of which is eighty times heavier than that of hydrogen, takes the place of hydrogen, it would seem that the whole system of dynamic equilibrium must be destroyed.

Without entering into the minute analysis of this question, I think it will be sufficient to examine it by the light of two well-known phenomena, one of which will be found in the department of chemistry and the other in that of celestial mechanics, and both will serve to demonstrate the existence of that unity in the plan of creation which is a consequence of the Newtonian doctrines. Experiments demonstrate that when a heavy element is substituted for a light one in a chemical compound—for example, for magnesium, in the oxide of that metal, an atom of mercury, which is 8⅓ times heavier—the chief chemical characteristics or properties are generally, though not always, preserved.

The substitution of silver for hydrogen, than which it is 108 times heavier, does not affect all the properties of the substance, though it does some. Therefore chemical substitutions of this kind—the substitution of light for heavy atoms—need not necessarily entail changes in the original equilibrium; and this point is still further elucidated by the consideration that the periodic law indicates the degree of influence of an increment of weight in the atom as affecting the possible equilibria, and also what degree of increase in the weight of the atoms reproduces some, though not all, of the properties of the substance.

This tendency to repetition—these periods—may be likened to those annual or diurnal periods with which we are so familiar on the earth. Days and years follow each other, but, as they do so, many things change; and in like manner chemical evolutions, changes in the masses of the elements, permit of much remaining undisturbed, though many properties undergo alteration. The system is maintained according to the laws of conservation in nature, but the motions are altered in consequence of the change of parts.

Next, let us take an astronomical case—such, for example, as the earth and the moon—and let us imagine that the mass of the latter is constantly increasing. The question is, what will then occur? The path of the moon in space is a wave-line similar to that which geometricians have named epicycloidal, or the locus of a point in a circle rolling round another circle. But in consequence of the influence of the moon it is evident that the path of the earth itself cannot be a geometric ellipse, even supposing the sun to be immovably fixed; it must be an epicycloidal curve, though not very far removed from the true ellipse—that is to say, it will be impressed with but faint undulations. It is only the common centre of gravity of the earth and the moon which describes a true ellipse round the sun. If the moon were to increase, the relative undulations of the earth's path would increase in amplitude, those of the moon would also change, and when the mass of the moon had increased to an equality with that of the earth, the path would consist of epicycloidal curves crossing each other and having opposite phases. But a similar relation exists between the sun and the earth, because the former is also moving in space. We may apply these views to the world of atoms, and suppose that in their movements, when heavy ones take the place of those that are lighter, similar changes take place, provided that the system or the molecule is preserved throughout the change.

It seems probable that in the heavenly systems, during incalculable astronomical periods, changes have taken place and are still going on similar to those which pass rapidly before our eyes during the chemical reaction of molecules, and the progress of molecular mechanics may—we hope will—in course of time permit us to explain those changes in the stellar world which have more than once been noticed by astronomers, and which are now so carefully studied. A coming Newton will discover the laws of these changes. Those laws, when applied to chemistry, may exhibit peculiarities, but these will certainly be mere variations on the grand harmonious theme which reigns in nature. The discovery of the laws which produce this harmony in chemical evolution will only be possible, it seems to me, under the banner of Newtonian dynamics, which has so long waved over the domains of mechanics, astronomy, and physics. In calling chemists to take their stand under its peaceful and catholic shadow I imagine that I am aiding in establishing that scientific union which the managers of the Royal Institution wish to effect, who have shown their desire to do so by the flattering invitation which has given me—a Russian—the opportunity of laying before the countrymen of Newton an attempt to apply to chemistry one of his immortal principles.

APPENDIX II

THE PERIODIC LAW OF THE CHEMICAL ELEMENTS

By PROFESSOR MENDELÉEFF

FARADAY LECTURE DELIVERED BEFORE THE FELLOWS OF
THE CHEMICAL SOCIETY IN THE THEATRE OF THE ROYAL INSTITUTION
ON TUESDAY, JUNE 4, 1889

THE high honour bestowed by the Chemical Society in inviting me to pay a tribute to the world-famed name of Faraday by delivering this lecture has induced me to take for its subject the Periodic Law of the Elements, this being a generalisation in chemistry which has of late attracted much attention.

While science is pursuing a steady onward movement, it is convenient from time to time to cast a glance back on the route already traversed, and especially to consider the new conceptions which aim at discovering the general meaning of the stock of facts accumulated from day to day in our laboratories. Owing to the possession of laboratories, modern science now bears a new character, quite unknown, not only to antiquity, but even to the preceding century. Bacon's and Descartes' idea of submitting the mechanism of science simultaneously to experiment and reasoning has been fully realised in the case of chemistry, it having become not only possible but always customary to experiment. Under the all-penetrating control of experiment, a new theory, even if crude, is quickly strengthened, provided it be founded on a sufficient basis; the asperities are removed, it is amended by degrees, and soon loses the phantom light of a shadowy form or of one founded on mere prejudice; it is able to lead to logical conclusions, and to submit to experimental proof. Willingly or not, in science we all must submit not to what seems to us attractive from one point of view or from another, but to what represents an agreement between theory and experiment; in other words, to demonstrated generalisation and to the approved experiment. Is it long since many refused to accept the generalisations involved in the law of Avogadro and Ampère, so widely extended by Gerhardt? We still may hear the voices of its opponents; they enjoy perfect freedom, but vainly will their voices rise so long as they do not use the language of demonstrated facts. The striking observations with the spectroscope which have permitted us to analyse the chemical constitution of distant worlds seemed, at first, applicable to the task of determining the nature of the atoms themselves; but the working out of the idea in the laboratory soon demonstrated that the characters of spectra are determined, not directly by the atoms, but by the molecules into which the atoms are packed; and so it became evident that more verified facts must be collected before it will be possible to formulate new generalisations capable of taking their place beside those ordinary ones based upon the conception of simple substances and atoms. But as the shade of the leaves and roots of living plants, together with the relics of a decayed vegetation, favour the growth of the seedling and serve to promote its luxuriant development, in like manner sound generalisations—together with the relics of those which have proved to be untenable—promote scientific productivity, and ensure the luxuriant growth of science under the influence of rays emanating from the centres of scientific energy. Such centres are scientific associations and societies. Before one of the oldest and most powerful of these I am about to take the liberty of passing in review the twenty years' life of a generalisation which is known under the name of the Periodic Law. It was in March 1869 that I ventured to lay before the then youthful Russian Chemical Society the ideas upon the same subject which I had expressed in my just written 'Principles of Chemistry.'

Without entering into details, I shall give the conclusions I then arrived at in the very words I used:—

'1. The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

'2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (e.g., platinum, iridium, osmium) or which increase regularly (e.g., potassium, rubidium, cæsium).

'3. The arrangement of the elements, or of groups of elements, in the order of their atomic weights, corresponds to their so-called *valencies* as well as, to some extent, to their distinctive chemical properties—as is apparent, among other series, in that of lithium, beryllium, barium, carbon, nitrogen, oxygen, and iron.

'4. The elements which are the most widely diffused have *small* atomic weights.

'5. The *magnitude* of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound.

'6. We must expect the discovery of many yet *unknown* elements—for example, elements analogous to aluminium and silicon, whose atomic weight would be between 65 and 75.

'7. The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus, the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.

'8. Certain characteristic properties of the elements can be foretold from their atomic weights.

'The aim of this communication will be fully attained if I succeed in drawing the attention of investigators to those relations which exist between the atomic weights of dissimilar elements, which, so far as I know, have hitherto been almost completely neglected. I believe that the solution of some of the most important problems of our science lies in researches of this kind.'

To-day, twenty years after the above conclusions were formulated, they may still be considered as expressing the essence of the now well-known periodic law.

Reverting to the epoch terminating with the sixties, it is proper to indicate three series of data without the knowlege of which the periodic law could not have been discovered, and which rendered its appearance natural and intelligible.

In the first place, it was at that time that the numerical value of atomic weights became definitely known. Ten years earlier such knowledge did not exist, as may be gathered from the fact that in 1860 chemists from all parts of the world met at Karlsruhe in order to come to some agreement, if not with respect to views relating to atoms, at any rate as regards their definite representation. Many of those present probably remember how vain were the hopes of coming to an understanding, and how much ground was gained at that Congress by the followers of the unitary theory so brilliantly represented by Cannizzaro. I vividly remember the impression produced by his speeches, which admitted of no compromise, and seemed to advocate truth itself, based on the conceptions of Avogadro, Gerhardt, and Regnault, which at that time were far from being generally recognised. And though no understanding could be arrived at, yet the objects of the meeting were attained, for the ideas of Cannizzaro proved, after a few years, to be the only ones which could stand criticism, and which represented an atom as 'the smallest portion of an element which enters into a molecule of its compound.' Only such real atomic weights—not conventional ones—could afford a basis for generalisation. It is sufficient, by way of example, to indicate the following cases in which the relation is seen at once and is perfectly clear:—

K = 39 Rb = 85 Cs = 133
Ca = 40 Sr = 87 Ba = 137

whereas with the equivalents then in use—

K = 39 Rb = 85 Cs = 133
Ca = 20 Sr = 43·5 Ba = 68·5

the consecutiveness of change in atomic weight, which with the true values is so evident, completely disappears.

Secondly, it had become evident during the period 1860–1870, and even during the preceding decade, that the relations between the atomic weights of analogous elements were governed by some general and simple laws. Cooke, Cremers, Gladstone, Gmelin, Lenssen, Pettenkofer, and especially Dumas, had already established many facts bearing on that view. Thus Dumas compared the following groups of analogous elements with organic radicles:—

	Diff.		Diff.		Diff.		Diff.
		Mg = 12		P = 31		O = 8	
			8		44		8
Li = 7		Ca = 20		As = 75		S = 16	
	16		3 × 8		44		3 × 8
Na = 23		Sr = 44		Sb = 119		Se = 40	
	16		3 × 8		2 × 44		3 × 8
K = 39		Ba = 68		Bi = 207		Te = 64	

and pointed out some really striking relationships, such as the following:—

$\mathrm{F} = 19.$
$\mathrm{Cl} = 35{\cdot}5 = 19 + 16{\cdot}5.$
$\mathrm{Br} = 80 = 19 + 2 \times 16{\cdot}5 + 28.$
$\mathrm{I} = 127 = 2 \times 19 + 2 \times 16{\cdot}5 + 2 \times 28.$

A. Strecker, in his work 'Theorien und Experimente zur Bestimmung der Atomgewichte der Elemente' (Braunschweig, 1859), after summarising the data relating to the subject, and pointing out the remarkable series of equivalents—

$\mathrm{Cr} = 26{\cdot}2 \quad \mathrm{Mn} = 27{\cdot}6 \quad \mathrm{Fe} = 28 \quad \mathrm{Ni} = 29 \quad \mathrm{Co} = 30 \quad \mathrm{Cu} = 31{\cdot}7$
$\mathrm{Zn} = 32{\cdot}5$

remarks: 'It is hardly probable that all the above-mentioned relations between the atomic weights (or equivalents) of chemically analogous elements are merely accidental. We must, however, leave to the future the discovery of the *law* of the relations which appears in these figures.'[1]

In such attempts at arrangement and in such views are to be recognised the real forerunners of the periodic law; the ground was prepared for it beween 1860 and 1870, and that it was not expressed in a determinate form before the end of the decade may, I suppose, be ascribed to the fact that only analogous elements had been compared. The idea of seeking for a relation between the atomic weights of all the elements was foreign to the ideas then current, so that neither the *vis tellurique* of De Chancourtois, nor *law of octaves* of Newlands, could secure anybody's attention. And yet both De Chancourtois and Newlands, like Dumas and Strecker, more than Lenssen and Pettenkofer, had made an approach to the periodic law and had discovered its germs. The solution of the problem advanced but slowly, because the facts, but not the law, stood foremost in all attempts; and the law could not awaken a general interest so long as elements, having no apparent connection with each other, were included in the same octave; as, for example:—

1st octave of Newlands . .	H	F	Cl	Co & Ni	Br	Pd	I	Pt & Ir
7th Ditto	O	S	Fe	Se	Rh & Ru	Te	Au	Os or Th

Analogies of the above order seemed quite accidental, and the more so as the octave contained occasionally ten elements instead of eight, and when two

---

[1] 'Es ist wohl kaum anzunehmen, dass alle im vorhergehenden hervorgehobenen Beziehungen zwischen den Atomgewichten (oder Aequivalenten) in chemischen Verhältnissen einander ähnliche Elemente bloss zufällig sind. Die Auffindung der in diesen Zahlen *gesetzlichen* Beziehungen müssen wir jedoch der Zukunft überlassen.'

such elements as Ba and V, Co and Ni, or Rh and Ru, occupied one place in the octave.[2] Nevertheless, the fruit was ripening, and I now see clearly that Strecker, De Chancourtois, and Newlands stood foremost in the way towards the discovery of the periodic law, and that they merely wanted the boldness necessary to place the whole question at such a height that its reflection on the facts could be clearly seen.

A third circumstance which revealed the periodicity of chemical elements was the accumulation, by the end of the sixties, of new information respecting the rare elements, disclosing their many-sided relations to the other elements and to each other. The researches of Marignac on niobium, and those of Roscoe on vanadium, were of special moment. The striking analogies between vanadium and phosphorus on the one hand, and between vanadium and chromium on the other, which became so apparent in the investigations connected with that element, naturally induced the comparison of $V = 51$ with $Cr = 52$, $Nb = 94$ with $Mo = 96$, and $Ta = 192$ with $W = 194$; while, on the other hand, $P = 31$ could be compared with $S = 32$, $As = 75$ with $Se = 79$, and $Sb = 120$ with $Te = 125$. From such approximations there remained but one step to the discovery of the law of periodicity.

The law of periodicity was thus a direct outcome of the stock of generalisations and established facts which had accumulated by the end of the decade 1860–1870; it is an embodiment of those data in a more or less systematic expression. Where, then, lies the secret of the special importance which has since been attached to the periodic law, and has raised it to the position of a generalisation which has already given to chemistry unexpected aid, and which promises to be far more fruitful in the future and to impress upon several branches of chemical research a peculiar and original stamp? The remaining part of my communication will be an attempt to answer this question.

In the first place we have the circumstance that, as soon as the law made its appearance, it demanded a revision of many facts which were considered by chemists as fully established by existing experience. I shall return, later on, briefly to this subject, but I wish now to remind you that the periodic law, by insisting on the necessity for a revision of supposed facts, exposed itself at once to destruction in its very origin. Its first requirements, however, have been almost entirely satisfied during the last 20 years; the supposed facts have yielded to the law, thus proving that the law itself was a legitimate induction from the verified facts. But our inductions from data have often to do with such details of a science so rich in facts that only generalisations which cover a wide range of important phenomena can attract general attention. What were the regions touched on by the periodic law? This is what we shall now consider.

The most important point to notice is, that periodic functions, used for the purpose of expressing changes which are dependent on variations of time and space, have been long known. They are familiar to the mind when we have to deal with motion in closed cycles, or with any kind of deviation from

---

[2] To judge from J. A. R. Newlands's work, *On the Discovery of the Periodic Law*, London, 1884, p. 149; 'On the Law of Octaves' (from the *Chemical News*, 12, 83, August 18, 1865).

a stable position, such as occurs in pendulum-oscillations. A like periodic function became evident in the case of the elements, depending on the mass of the atom. The primary conception of the masses of bodies, or of the masses of atoms, belongs to a category which the present state of science forbids us to discuss, because as yet we have no means of dissecting or analysing the conception. All that was known of functions dependent on masses derived its origin from Galileo and Newton, and indicated that such functions either decrease or increase with the increase of mass, like the attraction of celestial bodies. The numerical expression of the phenomena was always found to be proportional to the mass, and in no case was an increase of mass followed by a recurrence of properties such as is disclosed by the periodic law of the elements. This constituted such a novelty in the study of the phenomena of nature that, although it did not lift the veil which conceals the true conception of mass, it nevertheless indicated that the explanation of that conception must be searched for in the masses of the atoms; the more so as all masses are nothing but aggregations, or additions, of chemical atoms which would be best described as chemical individuals. Let me remark, by the way, that though the Latin word 'individual' is merely a translation of the Greek word 'atom,' nevertheless history and custom have drawn a sharp distinction between the two words, and the present chemical conception of atoms is nearer to that defined by the Latin word than by the Greek, although this latter also has acquired a special meaning which was unknown to the classics. The periodic law has shown that our chemical individuals display an harmonic periodicity of properties dependent on their masses. Now natural science has long been accustomed to deal with periodicities observed in nature, to seize them with the vice of mathematical analysis, to submit them to the rasp of experiment. And these instruments of scientific thought would surely, long since, have mastered the problem connected with the chemical elements, were it not for a new feature which was brought to light by the periodic law, and which gave a peculiar and original character to the periodic function.

If we mark on an axis of abscissæ a series of lengths proportional to angles, and trace ordinates which are proportional to sines or other trigonometrical functions, we get periodic curves of an harmonic character. So it might seem, at first sight, that with the increase of atomic weights the function of the properties of the elements should also vary in the same harmonious way. But in this case there is no such continuous change as in the curves just referred to, because the periods do not contain the infinite number of points constituting a curve, but a *finite* number only of such points. An example will better illustrate this view. The atomic weights—

$$\mathrm{Ag} = 108 \quad \mathrm{Cd} = 112 \quad \mathrm{In} = 113 \quad \mathrm{Sn} = 118 \quad \mathrm{Sb} = 120$$
$$\mathrm{Te} = 125 \quad \mathrm{I} = 127$$

steadily increase, and their increase is accompanied by a modification of many properties which constitutes the essence of the periodic law. Thus, for example, the densities of the above elements decrease steadily, being respectively—

10·5 8·6 7·4 7·2 6·7 6·4 4·9

while their oxides contain an increasing quantity of oxygen—

Ag_2O Cd_2O_2 In_2O_3 Sn_2O_4 Sb_2O_5 Te_2O_6 I_2O_7

But to connect by a curve the summits of the ordinates expressing any of these properties would involve the rejection of Dalton's law of multiple proportions. Not only are there no intermediate elements between silver, which gives AgCl, and cadmium, which gives $CdCl_2$, but, according to the very essence of the periodic law, there can be none ; in fact, a uniform curve would be inapplicable in such a case, as it would lead us to expect elements possessed of special properties at any point of the curve. The periods of the elements have thus a character very different from those which are so simply represented by geometers. They correspond to points, to numbers, to sudden changes of the masses, and not to a continuous evolution. In these sudden changes destitute of intermediate steps or positions, in the absence of elements intermediate between, say, silver and cadmium, or aluminium and silicon, we must recognise a problem to which no direct application of the analysis of the infinitely small can be made. Therefore, neither the trigonometrical functions proposed by Ridberg and Flavitzky, nor the pendulum-oscillations suggested by Crookes, nor the cubical curves of the Rev. Mr. Haughton, which have been proposed for expressing the periodic law, from the nature of the case, can represent the periods of the chemical elements. If geometrical analysis is to be applied to this subject, it will require to be modified in a special manner. It must find the means of representing in a special way, not only such long periods as that comprising

K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br,

but short periods like the following—

Na Mg Al Si P S Cl.

In the theory of numbers only do we find problems analogous to ours, and two attempts at expressing the atomic weights of the elements by algebraic formulæ seem to be deserving of attention, although neither of them can be considered as a complete theory, or as promising finally to solve the problem of the periodic law. The attempt of E. J. Mills (1886) does not even aspire to attain this end. He considers that all atomic weights can be expressed by a logarithmic function,

$$15(n - 0{\cdot}9375^t),$$

in which the variables n and t are *whole numbers*. Thus, for oxygen, $n = 2$, and $t = 1$, whence its atomic weight is $= 15{\cdot}94$; in the case of chlorine, bromine, and iodine, n has respective values of 3, 6, and 9, whilst $t = 7$, 6, and 9; in the case of potassium, rubidium, and cæsium, $n = 4$, 6, and 9, and $t = 14$, 18, and 20.

Another attempt was made in 1888 by B. N. Tchitchérin. Its author places the problem of the periodic law in the first rank, but as yet he has investigated the alkali metals only. Tchitchérin first noticed the simple relations existing between the atomic volumes of all alkali metals; they can be expressed, according to his views, by the formula

$$A(2-0{\cdot}00535An),$$

where A is the atomic weight, and n is equal to 8 for lithium and sodium, to 4 for potassium, to 3 for rubidium, and to 2 for cæsium. If n remained equal to 8 during the increase of A, the volume would become zero at $A=46\frac{2}{3}$, and it would reach its maximum at $A=23\frac{1}{3}$. The close approximation of the number $46\frac{2}{3}$ to the differences between the atomic weights of analogous elements (such as Cs – Rb, I – Br, and so on); the close correspondence of the number $23\frac{1}{3}$ to the atomic weight of sodium; the fact of n being necessarily a whole number, and several other aspects of the question, induce Tchitchérin to believe that they afford a clue to the understanding of the nature of the elements; we must, however, await the full development of his theory before pronouncing judgment on it. What we can at present only be certain of is this: that attempts like the two above named must be repeated and multiplied, because the periodic law has clearly shown that the masses of the atoms increase abruptly, by steps, which are clearly connected in some way with Dalton's law of multiple proportions; and because the periodicity of the elements finds expression in the transition from RX to RX_2, RX_3, RX_4, and so on till RX_8, at which point, the energy of the combining forces being exhausted, the series begins anew from RX to RX_2, and so on.

While connecting by new bonds the theory of the chemical elements with Dalton's theory of multiple proportions, or atomic structure of bodies, the periodic law opened for natural philosophy a new and wide field for speculation. Kant said that there are in the world 'two things which never cease to call for the admiration and reverence of man: the moral law within ourselves, and the stellar sky above us.' But when we turn our thoughts towards the nature of the elements and the periodic law, we must add a third subject, namely, 'the nature of the elementary individuals which we discover everywhere around us.' Without them the stellar sky itself is inconceivable; and in the atoms we see at once their peculiar individualities, the infinite multiplicity of the individuals, and the submission of their seeming freedom to the general harmony of Nature.

Having thus indicated a new mystery of Nature, which does not yet yield to rational conception, the periodic law, together with the revelations of spectrum analysis, have contributed to again revive an old but remarkably long-lived hope—that of discovering, if not by experiment, at least by a mental effort, the *primary matter*—which had its genesis in the minds of the Grecian philosophers, and has been transmited, together with many other ideas of the classic period, to the heirs of their civilisation. Having grown, during the times of the alchemists up to the period when experimental proof was required, the idea has rendered good service; it induced those careful observations and experiments which later on called into being the works of Scheele, Lavoisier, Priestley, and Cavendish. It then slumbered awhile, but was soon awakened by the attempts either to confirm or to refute the ideas of Prout as to the multiple-proportion relationship of the atomic weights of all the elements. And once again the inductive or experimental method of studying Nature gained a direct advantage from the old Pythagorean idea: because atomic weights were determined with an accuracy formerly unknown. But again the idea could not stand the ordeal of experimental test, yet the prejudice remains and has not been uprooted, even by Stas; nay, it has gained a new vigour, for we see that all which is imperfectly worked out, new and unexplained, from the still scarcely studied rare metals to the hardly perceptible nebulæ, has been used to justify it. As soon as spectrum analysis appears as a new and powerful weapon of chemistry, the idea of a primary matter is immediately attached to it. From all sides we see attempts to constitute the imaginary substance *helium*[3] the so much longed for primary matter. No attention is paid to the circumstance that the helium line is only seen in the spectrum of the solar protuberances, so that its universality in Nature remains as problematic as the primary matter itself; or to the fact that the helium line is wanting amongst the Fraunhofer lines of the solar spectrum, and thus does not answer to the brilliant fundamental conception which gives its real force to spectrum analysis.

And finally, no notice is taken even of the indubitable fact that the brilliancies of the spectral lines of the simple substances vary under different temperatures and pressures; so that all probabilities are in favour of the helium line simply belonging to some long since known element placed under such conditions of temperature, pressure, and gravity as have not yet been realised in our experiments. Again, the idea that the excellent investigations of Lockyer of the spectrum of iron can be interpreted in favour of the compound nature of that element evidently must have arisen from some misunderstanding. The spectrum of a compound certainly does not appear as a sum of the spectra of its components; and therefore the observations of Lockyer can be considered precisely as a proof that iron undergoes no other changes at the temperature of the sun than those which it experiences in the voltaic arc—provided the spectrum of iron is preserved. As to the shifting of some of the lines of the spectrum of iron while the other lines maintain their positions, it can be explained, as shown by M. Kleiber ('Journal of the Russian Chemical and Physical Society,' 1885, 147), by the relative motion of the various strata of the sun's atmosphere, and by Zöllner's laws of the relative brilliancies of different lines of the spectrum. Moreover, it ought not to be forgotten that if iron were really proved to consist of two or more unknown elements, we should simply have an increase in the number of our elements—not a reduction, and still less a reduction of all of them to one single primary matter.

Feeling that spectrum analysis will not yield a support to the Pythagorean conception, its modern promoters are so bent upon its being confirmed by the periodic law that the illustrious Berthelot, in his work 'Les Origines de l'Alchimie,' 1885, 313, has simply mixed up the fundamental idea of the law of periodicity with the ideas of Prout, the alchemists, and Democritus about primary matter.[4] But the periodic law, based as it is on the solid and whole-

---

[3] That is, a substance having a wave-length equal to 0·0005875 millimetre.

[4] He maintains (on p. 309) that the periodic law requires two new analogous elements, having atomic weights of 48 and 64, occupying positions between sulphur

some ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of a unique matter; and it has no historical connection with that relic of the torments of classical thought, and therefore it affords no more indication of the unity of matter or of the compound character of our elements than the law of Avogadro. or the law of specific heats, or even the conclusions of spectrum analysis. None of the advocates of a unique matter have ever tried to explain the law from the standpoint of ideas taken from a remote antiquity when it was found convenient to admit the existence of many gods—and of a unique matter.

When we try to explain the origin of the idea of a unique primary matter, we easily trace that in the absence of inductions from experiment it derives its origin from the scientifically philosophical attempt at discovering some kind of unity in the immense diversity of individualities which we see around. In classical times such a tendency could only be satisfied by conceptions about the immaterial world. As to the material world, our ancestors were compelled to resort to some hypothesis, and they adopted the idea of unity in the formative material, because they were not able to evolve the conception of any other possible unity in order to connect the multifarious relations of matter. Responding to the same legitimate scientific tendency, natural science has discovered throughout the universe a unity of plan, a unity of forces, and a unity of matter, and the convincing conclusions of modern science compel everyone to admit these kinds of unity. But while we admit unity in many things, we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere. It has been said of old, 'Give us a fulcrum, and it will become easy to displace the earth.' So also we must say, 'Give us something that is individualised, and the apparent diversity will be easily understood.' Otherwise, how could unity result in a multitude?

After a long and painstaking research, natural science has discovered the individualities of the chemical elements, and therefore it is now capable not only of analysing, but also of synthesising; it can understand and grasp generality and unity, as well as the individualised and the multifarious. The general and universal, like time and space, like force and motion, vary uniformly; the uniform admit of interpolations, revealing every intermediate phase. But the multitudinous, the individualised—such as ourselves, or the chemical elements, or the members of a peculiar periodic function of the elements, or Dalton's multiple proportions—is characterised in another way: we see in it, side by side with a connecting general principle, leaps, breaks of continuity, points which escape from the analysis of the infinitely small—an absence of complete intermediate links. Chemistry has found an answer to the question as to the causes of multitudes; and while retaining the conception of many elements, all submitted to the discipline of a general law, it offers an escape from the Indian Nirvana—the absorption in the universal, replacing it by the individualised. However, the place for individuality is so limited by the all-grasping, all-powerful universal,

and selenium, although nothing of the kind results from any of the different readings of the law.

that it is merely a point of support for the understanding of multitude in unity.

Having touched upon the metaphysical bases of the conception of a unique matter which is supposed to enter into the composition of all bodies, I think it necessary to dwell upon another theory, akin to the above conception—the theory of the compound character of the elements now admitted by some—and especially upon one particular circumstance which, being related to the periodic law, is considered to be an argument in favour of that hypothesis.

Dr. Pelopidas, in 1883, made a communication to the Russian Chemical and Physical Society on the periodicity of the hydrocarbon radicles, pointing out the remarkable parallelism which was to be noticed in the change of properties of hydrocarbon radicles and elements when classed in groups. Professor Carnelley, in 1886, developed a similar parallelism. The idea of M. Pelopidas will be easily understood if we consider the series of hydrocarbon radicles which contain, say, 6 atoms of carbon:—

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C_6H_{13}	C_6H_{12}	C_6H_{11}	C_6H_{10}	C_6H_9	C_6H_8	C_6H_7	C_6H_6

The first of these radicles, like the elements of the first group, combines with Cl, OH, and so on, and gives the derivatives of hexyl alcohol, C_6H_{13} (OH); but, in proportion as the number of hydrogen atoms decreases, the capacity of the radicles of combining with, say, the halogens increases. C_6H_{12} already combines with 2 atoms of chlorine; C_6H_{11} with 3 atoms, and so on. The last members of the series comprise the radicles of acids: thus C_6H_8, which belongs to the 6th group gives, like sulphur, a bibasic acid, $C_6H_8O_2(OH)_2$, which is homologous with oxalic acid. The parallelism can be traced still further, because C_6H_5 appears as a monovalent radicle of bezene, and with it begins a new series of aromatic derivatives, so analogous to the derivatives of the aliphatic series. Let me also mention another example from among those which have been given by M. Pelopidas. Starting from the alkaline radicle of monomethylammonium, $N(CH_3)H_3$, or NCH_6, which presents many analogies with the alkaline metals of the 1st group, he arrives, by successively diminishing the number of the atoms of hydrogen, at a 7th group which contains cyanogen, CN, which has long since been compared to the halogens of the 7th group.

The most important consequence which, in my opinion, can be drawn from the above comparison is that the periodic law, so apparent in the elements, has a wider application than might appear at first sight; it opens up a new vista of chemical evolutions. But, while admitting the fullest parallelism between the periodicity of the elements and that of the compound radicles, we must not forget that in the periods of the hydrocarbon radicles we have a *decrease* of mass as we pass from the representatives of the first group to the next, while in the periods of the elements the mass *increases* during the progression. It thus becomes evident that we cannot speak of an identity of periodicity in both cases, unless we put aside the ideas of mass and attraction, which are the real corner-stones of the whole of natural science, and even enter into those very conceptions of simple substances which came to light a full hundred years later than the immortal principles of Newton.[5]

From the foregoing, as well as from the failures of so many attempts at finding in experiment and speculation a proof of the compound character of the elements and of the existence of primordial matter, it is evident, in my opinion, that this theory must be classed among mere utopias. But utopias can only be combated by freedom of opinion, by experiment, and by new utopias. In the republic of scientific theories freedom of opinions is guaranteed. It is precisely that freedom which permits me to criticise openly the widely diffused idea as to the unity of matter in the elements. Experiments and attempts at confirming that idea have been so numerous that it really would be instructive to have them all collected together, if only to serve as a warning against the repetition of old failures. And now as to new utopias which may be helpful in the struggle against the old ones, I do not think it quite useless to mention a *fantasy* of one of my students who imagined that the weight of bodies does not depend upon their mass, but upon the character of the motion of their atoms. The atoms, according to this new utopian, may all be homogeneous or heterogeneous, we know not which; we know them in motion only, and that motion they maintain with the same persistence as the stellar bodies maintain theirs. The weights of atoms differ only in consequence of their various modes and quantity of motion; the heaviest atoms may be much simpler than the lighter ones: thus an atom of mercury may be simpler than an atom of hydrogen—the manner in which it moves causes it to be heavier. My interlocutor even suggested that the view which attributes the greater complexity to the lighter elements finds confirmation in the fact that the hydrocarbon radicles mentioned by Pelopidas, while becoming lighter as they lose hydrogen, change their properties periodically in the same manner as the elements change theirs, according as the atoms grow heavier.

The French proverb, *La critique est facile, mais l'art est difficile*, however, may well be reversed in the case of all such ideal views, as it is much easier to formulate than to criticise them. Arising from the virgin soil of newly established facts, the knowledge relating to the elements, to their masses, and to the periodic changes of their properties has given a motive for the formation of utopian hypothesis, probably because they could not be foreseen by the aid of any of the various metaphysical systems, and exist, like the idea of gravitation, as an independent outcome of natural science, requiring the acknowledgment of general laws, when these have been established with the same degree of persistency as is indispensable for the acceptance of a thoroughly established fact. Two centuries have elapsed since the theory of gravitation was enunciated, and although we do not understand its cause, we still must regard gravitation as a fundamental conception of natural philosophy, a conception which has enabled us to perceive much more than the metaphysicians did or could with their seeming omniscience. A hundred

---

[5] It is noteworthy that the year in which Lavoisier was born (1743)—the author of the idea of elements and of the indestructibility of matter—is later by exactly one century than the year in which the author of the theory of gravitation and mass was born (1643). The affiliation of the ideas of Lavoisier and those of Newton is beyond doubt.

years later the conception of the elements arose ; it made chemistry what it now is ; and yet we have advanced as little in our comprehension of simple substances since the times of Lavoisier and Dalton as we have in our understanding of gravitation. The periodic law of the elements is only twenty years old ; it is not surprising, therefore, that, knowing nothing about the causes of gravitation and mass, or about the nature of the elements, we do not comprehend the *rationale* of the periodic law. It is only by collecting established laws—that is, by working at the acquirement of truth—that we can hope gradually to lift the veil which conceals from us the causes of the mysteries of Nature and to discover their mutual dependency. Like the telescope and the microscope, laws founded on the basis of experiment are the instruments and means of enlarging our mental horizon.

In the remaining part of my communication I shall endeavour to show, and as briefly as possible, in how far the periodic law contributes to enlarge our range of vision. Before the promulgation of this law the chemical elements were mere fragmentary, incidental facts in Nature ; there was no special reason to expect the discovery of new elements, and the new ones which were discovered from time to time appeared to be possessed of quite novel properties. The law of periodicity first enabled us to perceive undiscovered elements at a distance which formerly was inaccessible to chemical vision ; and long ere they were discovered new elements appeared before our eyes possessed of a number of well-defined properties. We now know three cases of elements whose existence and properties were foreseen by the instrumentality of the periodic law. I need but mention the brilliant discovery of *gallium*, which proved to correspond to eka-aluminium of the periodic law, by Lecoq de Boisbaudran ; of *scandium*, corresponding to ekaboron, by Nilson ; and of *germanium*, which proved to correspond in all respects to ekasilicon, by Winkler. When, in 1871, I described to the Russian Chemical Society the properties, clearly defined by the periodic law, which such elements ought to possess, I never hoped that I should live to mention their discovery to the Chemical Society of Great Britain as a confirmation of the exactitude and the generality of the periodic law. Now that I have had the happiness of doing so, I unhesitatingly say that, although greatly enlarging our vision, even now the periodic law needs further improvements in order that it may become a trustworthy instrument in further discoveries.[6]

I shall venture to allude to some other matters which chemistry has discerned by means of its new instrument, and which it could not have made

---

[6] I foresee some more new elements, but not with the same certitude as before. I shall give one example, and yet I do not see it quite distinctly. In the series which contains Hg = 204, Pb = 206, and Bi = 208, we can imagine the existence (at the place VI—11) of an element analogous to tellurium, which we can describe as dvi-tellurium, Dt, having an atomic weight of 212, and the property of forming the oxide DtO_3. If this element really exists, it ought in the free state to be an easily fusible, crystalline, non-volatile metal of a grey colour, having a density of about 9·3, capable of giving a dioxide, DtO_2, equally endowed with feeble acid and basic properties. This dioxide must give on active oxidation an unstable higher oxide, DtO_3, which should resemble in its properties PbO_2 and Bi_2O_5. Dvi-tellurium hydride, if it be found to exist, will be a less stable compound than even H_2Te. The compounds of dvi-tellurium will be easily reduced, and it will form characteristic definite alloys with other metals.

out without a knowledge of the law of periodicity, and I shall confine myself to simple substances and to oxides.

Before the periodic law was formulated the atomic weights of the elements were purely empirical numbers, so that the magnitude of the equivalent, and the atomicity, or the value in substitution possessed by an atom, could only be tested by critically examining the methods of determination, but never directly by considering the numerical values themselves; in short, we were compelled to move in the dark, to submit to the facts, instead of being masters of them. I need not recount the methods which permitted the periodic law at last to master the facts relating to atomic weights, and I would merely call to mind that it compelled us to modify the valencies of *indium* and *cerium*, and to assign to their compounds a different molecular composition. Determinations of the specific heats of these two metals fully confirmed the change. The trivalency of *yttrium*, which makes us now represent its oxide as Y_2O_3 instead of as YO, was also foreseen (in 1870) by the periodic law, and it has now become so probable that Clève, and all other subsequent investigators of the rare metals, have not only adopted it, but have also applied it without any new demonstration to substances so imperfectly known as those of the cerite and gadolinite group, especially since Hillebrand determined the specific heats of lanthanum and didymium and confirmed the expectations suggested by the periodic law. But here, especially in the case of didymium we meet with a series of difficulties long since foreseen through the periodic law, but only now becoming evident, and chiefly arising from the relative rarity and insufficient knowledge of the elements which usually accompany didymium.

Passing to the results obtained in the case of the rare elements *beryllium*, *scandium*, and *thorium*, it is found that these have many points of contact with the periodic law. Although Avdéeff long since proposed the magnesia formula to represent beryllium oxide, yet there was so much to be said in favour of the alumina formula, on account of the specific heat of the metals and the isomorphism of the two oxides, that it became generally adopted and seemed to be well established. The periodic law, however, as Brauner repeatedly insisted ('Berichte,' 1878, 872; 1881, 53), was against the formula Be_2O_3; it required the magnesia formula BeO—that is, an atomic weight of 9—because there was no place in the system for an element like beryllium having an atomic weight of 13·5. This divergence of opinion lasted for years, and I often heard that the question as to the atomic weight of beryllium threatened to disturb the generality of the periodic law, or, at any rate, to require some important modifications of it. Many forces were operating in the controversy regarding beryllium, evidently because a much more important question was at issue than merely that involved in the discussion of the atomic weight of a relatively rare element: and during the controversy the periodic law became better understood, and the mutual relations of the elements became more apparent than ever before. It is most remarkable that the victory of the periodic law was won by the researches of the very observers who previously had discovered a number of facts in support of the trivalency of beryllium. Applying the higher law of Avogadro, Nilson and Potterson have finally shown that the density of the vapour of the beryllium chloride, $BeCl_2$, obliges us to regard beryllium as bivalent in conformity with the periodic law.[7] I consider the confirmation of Avdéeff's and Brauner's view as important in the history of the periodic law as the discovery of scandium, which, in Nilson's hands, confirmed the existence of ekaboron.

The circumstance that *thorium* proved to be quadrivalent, and Th = 232, in accordance with the views of Chydenius and the requirements of the periodic law, passed almost unnoticed, and was accepted without opposition, and yet both thorium and uranium are of great importance in the periodic system, as they are its last members, and have the highest atomic weights of all the elements.

The alteration of the atomic weight of *uranium* from U = 120 into U = 240 attracted more attention, the change having been made on account of the periodic law, and for no other reason. Now that Roscoe, Rammelsberg, Zimmermann, and several others have admitted the various claims of the periodic law in the case of uranium, its high atomic weight is received without objection, and it endows that element with a special interest.

While thus demonstrating the necessity for modifying the atomic weights of several insufficiently known elements, the periodic law enabled us also to detect errors in the determination of the atomic weights of several elements whose valencies and true position among other elements were already well known. Three such cases are especially noteworthy: those of tellurium, titanium, and platinum. Berzelius had determined the atomic weight of *tellurium* to be 128, while the periodic law claimed for it an atomic weight below that of iodine, which had been fixed by Stas at 126·5, and which was certainly not higher than 127. Brauner then undertook the investigation, and he has shown that the true atomic weight of tellurium is lower than that of iodine, being near to 125. For *titanium*, the extensive researches of Thorpe have confirmed the atomic weight of Ti = 48, indicated by the law and already foreseen by Rose, but contradicted by the analyses of Pierre and several other chemists. An equally brilliant confirmation of the expectations based on the periodic law has been given in the case of the series osmium, iridium, platinum, and gold. At the time of the promulgation of the periodic law, the determinations of Berzelius, Rose, and many others gave the following figures:—

$$Os = 200;\ Ir = 197;\ Pt = 198;\ Au = 196.$$

---

[7] Let me mention another proof of the bivalency of beryllium which may have passed unnoticed, as it was only published in the Russian chemical literature. Having remarked (in 1884) that the density of such solutions of chlorides of metals, MCl_n, as contain 200 mols. of water (or a large and constant amount of water) regularly increases as the molecular weight of the dissolved salt increases, I proposed to one of our young chemists, M. Burdakoff, that he should investigate beryllium chloride. If its molecule be $BeCl_2$ its weight must be = 80; and in such a case it must be heavier than the molecule of $KCl = 74·5$, and lighter than that of $MgCl_2 = 93$. On the contrary, if beryllium chloride is a trichloride, $BeCl_3 = 120$, its molecule must be heavier than that of $CaCl_2 = 111$, and lighter than that of $MnCl_2 = 126$. Experiment has shown the correctness of the former formula, the solution $BeCl_2 + 200H_2O$ having (at 15°/4°) a density of 1·0138, this being a higher density than that of the solution $KCl + 200H_2O$ (= 1·0121), and lower than that of $MgCl_2 + 200H_2O$ (= 1·0203). The bivalency of beryllium was thus confirmed in the case of both the dissolved and the vaporised chloride.

The expectations of the periodic law[8] have been confirmed, first, by new determinations of the atomic weight of *platinum* (by Seubert, Dittmar, and M'Arthur, which proved to be near to 196 (taking $O=16$, as proposed by Marignac, Brauner, and others); secondly, by Seubert having proved that the atomic weight of *osmium* is really lower than that of platinum, being near to 191; and thirdly, by the investigations of Krüss, Thorpe, and Laurie, proving that the atomic weight of *gold* exceeds that of platinum, and approximates to 197. The atomic weights which were thus found to require correction were precisely those which the periodic law had indicated as affected with errors; and it has been proved, therefore, that the periodic law affords a means of testing experimental results. If we succeed in discovering the exact character of the periodic relationships between the increments in atomic weights of allied elements discussed by Ridberg in 1885, and again by Bazaroff in 1887, we may expect that our instrument will give us the means of still more closely controlling the experimental data relating to atomic weights.

Let me next call to mind that, while disclosing the variation of chemical properties,[9] the periodic law has also enabled us to systematically discuss many of the physical properties of elementary bodies, and to show that these properties are also subject to the law of periodicity. At the Moscow Congress of Russian Naturalists in August 1869 I dwelt upon the relations which existed between density and the atomic weight of the elements. The following year Professor Lothar Meyer, in his well-known paper,[10] studied the same subject in more detail, and thus contributed to spread information about the periodic law. Later on, Carnelley, Laurie, L. Meyer, Roberts-Austen, and several others applied the periodic system to represent the order in the changes of the magnetic properties of the elements, their melting-points, the heats of formation of their haloid compounds, and even of such mechanical properties as the coefficient of elasticity, the breaking stress, &c., &c. These deductions, which have received further support in the discovery of new elements endowed not only with chemical but even with physical properties, which were foreseen by the law of periodicity, are well known; so I need not dwell upon the subject, and may pass to the consideration of oxides.[11]

---

[8] I pointed them out in the *Liebig's Annalen*, Supplement Band viii. 1871, p. 211.

[9] Thus, in the typical small period of

Li, Be, B, C, N, O, F,

we see at once the progression from the alkali metals to the acid non-metals, such as are the halogens.

[10] *Liebig's Annalen*, Supplement Band vii. 1870.

[11] A distinct periodicity can also be discovered in the spectra of the elements. Thus the researches of Hartley, Ciamician, and others have disclosed, first, the homology of the spectra of analogous elements; secondly, that the alkali metals have simpler spectra than the metals of the following groups; and thirdly, that there is a certain likeness between the complicated spectra of manganese and iron on the one hand, and the no less complicated spectra of chlorine and bromine on the other hand, and their likeness corresponds to the degree of analogy between those elements which is indicated by the periodic law.

In indicating that the gradual increase of the power of elements of combining with oxygen is accompanied by a corresponding decrease in their power of combining with hydrogen, the periodic law has shown that there is a limit of oxidation, just as there is a well-known limit to the capacity of elements for combining with hydrogen. A single atom of an element combines with at most four atoms of either hydrogen or oxygen; and while CH_4 and SiH_4 represent the highest hydrides, so RuO_4 and OsO_4 are the highest oxides. We are thus lead to recognise types of oxides, just as we have had to recognise types of hydrides.[12]

The periodic law has demonstrated that the maximum extent to which different non-metals enter into combination with oxygen is determined by the extent to which they combine with hydrogen, and that the sum of the number of equivalents of both must be equal to 8. Thus chlorine, which combines with 1 atom or 1 equivalent of hydrogen, cannot fix more than 7 equivalents of oxygen, giving Cl_2O_7; while sulphur, which fixes 2 equivalents of hydrogen, cannot combine with more than 6 equivalents or 3 atoms of oxygen. It thus becomes evident that we cannot recognise as a fundamental property of the elements the atomic valencies deduced from their hydrides; and that we must modify, to a certain extent, the theory of atomicity if we desire to raise it to the dignity of a general principle capable of affording an insight into the constitution of all compound molecules. In other words, it is only to carbon, which is quadrivalent with regard both to oxygen and hydrogen, that we can apply the theory of constant valency and of bond, by means of which so many still endeavour to explain the structure of compound molecules. But I should go too far if I ventured to explain in detail the conclusions which can be drawn from the above considerations. Still, I think it necessary to dwell upon one particular fact which must be explained from the point of view of the periodic law in order to clear the way to its extension in that particular direction.

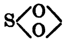
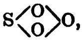
The higher oxides yielding salts the formation of which was foreseen by the periodic system—for instance, in the short series beginning with sodium—

$$Na_2O,\ MgO,\ Al_2O_3,\ SiO_2,\ P_2O_5,\ SO_3,\ Cl_2O_7,$$

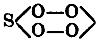
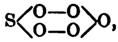
must be clearly distinguished from the higher degrees of oxidation which correspond to hydrogen peroxide and bear the true character of peroxides. Peroxides such as Na_2O_2, BaO_2, and the like have long been known. Similar

---

[12] Formerly it was supposed that, being a bivalent element, oxygen can enter into any grouping of the atoms, and there was no limit foreseen as to the extent to which it could further enter into combination. We could not explain why bivalent sulphur, which forms compounds such as


and

,

could not also form oxides such as—


or

,

while other elements, as, for instance, chlorine, form compounds such as—

Cl—O—O—O—O—K

peroxides have also recently become known in the case of chromium, sulphur, titanium, and many other elements, and I have sometimes heard it said that discoveries of this kind weaken the conclusions of the periodic law in so far as it concerns the oxides. I do not think so in the least, and I may remark, in the first place, that all these peroxides are endowed with certain properties obviously common to all of them, which distinguish them from the actual, higher, salt-forming oxides, especially their easy decomposition by means of simple contact agencies; their incapability of forming salts of the common type; and their capability of combining with other peroxides (like the faculty which hydrogen peroxide possesses of combining with barium peroxide, discovered by Schoene). Again, we remark that some groups are especially characterised by their capacity of generating peroxides. Such is, for instance, the case in the sixth group, where we find the well-known peroxides of sulphur, chromium, and uranium; so that further investigation of peroxides will probably establish a new periodic function, foreshadowing that molybdenum and tungsten will assume peroxide forms with comparative readiness. To appreciate the constitution of such peroxides, it is enough to notice that the peroxide form of sulphur (so-called persulphuric acid) stands in the same relation to sulphuric acid as hydrogen peroxide stands to water:—

$$H(OH), \text{ or } H_2O, \text{ responds to } (OH)(OH), \text{ or } H_2O_2,$$

and so also—

$$H(HSO_4), \text{ or } H_2SO_4, \text{ responds to } (HSO_4)(HSO_4), \text{ or } H_2S_2O_8.$$

Similar relations are seen everywhere, and they correspond to the principle of substitutions which I long since endeavoured to represent as one of the chemical generalisations called into life by the periodic law. So also sulphuric acid, if considered with reference to hydroxyl, and represented as follows—

$$HO(SO_2OH),$$

has its corresponding compound in dithionic acid—

$$(SO_2OH)(SO_2OH), \text{ or } H_2S_2O_6.$$

Therefore, also, phosphoric acid, $HO(POH_2O_2)$, has, in the same sense, its corresponding compound in the subphosphoric acid of Saltzer:—

$$(POH_2O_2)(POH_2O_2), \text{ or } H_4P_2O_6;$$

and we must suppose that the peroxide compound corresponding to phosphoric acid, if it be discovered, will have the following structure:—

$$(H_2PO_4)_2 \text{ or } H_4P_2O_8 = 2H_2O + 2PO_3.^{13}$$

So far as is known at present, the highest form of peroxides is met with in

---

[13] In this sense, oxalic acid, $(COOH)_2$, also corresponds to carbonic acid, $OH(COOH)$, in the same way that dithionic acid corresponds to sulphuric acid, and subphosphoric acid to phosphoric; hence, if a peroxide corresponding to carbonic acid be obtained, it will have the structure of $(HCO_3)_2$, or $H_2C_2O_6 = H_2O + C_2O_5$. So also lead must have a real peroxide, Pb_2O_5.

the peroxide of uranium, UO_4, prepared by Fairley;[14] while OsO_4 is the highest oxide giving salts. The line of argument which is inspired by the periodic law, so far from being weakened by the discovery of peroxides, is thus actually strengthened, and we must hope that a further exploration of the region under consideration will confirm the applicability to chemistry generally of the principles deduced from the periodic law.

Permit me now to conclude my rapid sketch of the oxygen compounds by the observation that the periodic law is especially brought into evidence in the case of the oxides which constitute the immense majority of bodies at our disposal on the surface of the earth.

The oxides are evidently subject to the law, both as regards their chemical and their physical properties, especially if we take into account the cases of polymerism which are so obvious when comparing CO_2 with Si_nO_{2n}. In order to prove this I give the densities *s* and the specific volumes *v* of the higher oxides of two short periods. To render comparison easier, the oxides are all represented as of the form R_2O_n. In the column headed Δ the differences are given between the volume of the oxygen compound and that of the parent element divided by *n*—that is, by the number of atoms of oxygen in the compound:[15]—

	s.	*v.*	Δ		*s.*	*v.*	Δ
Na_2O	2·6	24	−22	K_2O	2·7	35	−55
Mg_2O_2	3·6	22	− 3	Ca_2O	3·15	36	− 7
Al_2O_3	4·0	26	+ 1·3	Sc_2O_3	3·86	35	0
Si_2O_4	2·65	45	5·2	Li_2O_4	4·2	38	+ 5
P_2O_5	2·39	59	6·2	V_2O_5	3·49	52	6·7
S_2O_6	1·96	82	8·7	Cr_2O_6	2·74	73	9·5

I have nothing to add to these figures, except that like relations appear in other periods as well. The above relations were precisely those which made it possible for me to be certain that the relative density of ekasilicon oxide would be about 4·7; germanium oxide, actually obtained by Winkler, proved, in fact, to have the relative density 4·703.

The foregoing account is far from being an exhaustive one of all that has already been discovered by means of the periodic law telescope in the boundless realms of chemical evolution. Still less is it an exhaustive account of all that may yet be seen, but I trust that the little which I have said will account for the philosophical interest attached in chemistry to this law. Although

---

[14] The compounds of uranium prepared by Fairley seem to me especially instructive in understanding the peroxides. By the action of hydrogen peroxide on uranium oxide, UO_3, a peroxide of uranium, $UO_4,4H_2O$, is obtained ($U = 240$) if the solution be acid; but if hydrogen peroxide act on uranium oxide in the presence of caustic soda, a crystalline deposit is obtained which has the composition $Na_4UO_8,4H_2O$, and evidently is a combination of sodium peroxide, Na_2O_2, with uranium peroxide, UO_4. It is possible that the former peroxide, $UO_4,4H_2O$, contains the elements of hydrogen peroxide and uranium peroxide, U_2O_7, or even $U(OH)_6,H_2O_2$, like the peroxide of tin recently discovered by Spring, which has the constitution Sn_2O_5,H_2O_2.

[15] Δ thus represents the average increase of volume for each atom of oxygen contained in the higher salt-forming oxide. The acid oxides give, as a rule, a higher value of Δ, while in the case of the strongly alkaline oxides its value is usually negative.

but a recent scientific generalisation, it has already stood the test of laboratory verification, and appears as an instrument of thought which has not yet been compelled to undergo modification; but it needs not only new applications but also improvements, further development, and plenty of fresh energy. All this will surely come, seeing that such an assembly of men of science as the Chemical Society of Great Britain has expressed the desire to have the history of the periodic law described in a lecture dedicated to the glorious name of Faraday.

APPENDIX III

AN ATTEMPT TOWARDS A CHEMICAL CONCEPTION OF THE ETHER

BY PROFESSOR D. MENDELÉEFF

IN his 'Dictionnaire Complet,' P. Larousse defines the ether as 'an imponderable elastic fluid, filling space and forming the source of light, heat, electricity, &c.' This is laconic, but sufficient to raise some misgivings in the mind of a thoughtful man of science. He is obliged to admit, in the ether, the properties of a substance (fluid), while at the same time, in order to explain in some way the transmission of energy through space by its motion, the ether is assumed to be an all-pervading 'medium.' Moreover, in order to explain the phenomena of light, electricity, and even gravity, this medium is supposed to undergo various disturbances (perturbations) and changes in its structure (deformation), like those observed in solids, liquids, and gases. If the fluid medium permeates everything and everywhere, it cannot be said to have weight, just as the ponderability of air could not be recognised before the invention of the air-pump. Yet the ether must have weight, because, since the days of Galileo and Newton, the quality of gravitation or of weight forms a primary property of substances. From various considerations Lord Kelvin came to the conclusion that a cubic metre of ether should weigh about and not less than 0·000,000,000,000,000,1 grm., while a cubic metre of the lightest gas, hydrogen, weighs 90 grams under the atmospheric pressure. The above-mentioned misgivings of the thoughtful scientist begin in his most plausible endeavours to ascribe a certain weight or mass to the ether, for the question naturally arises: At what pressure and temperature will this weight be proper to ether? For at infinitely small pressures or exceedingly high temperatures, steam or hydrogen would have as small a density as that given by Lord Kelvin for the ether. And as regards the density of the ether in interplanetary space, neither steam nor hydrogen would have a measurable density in these regions, notwithstanding the extreme cold, for the pressure would be infinitely small. Theoretically, space may be supposed to be filled with such rarefied residues of vapours and gases. And this view even corresponds with Kant's and Laplace's and other theories, which strive to explain the unity of plan in the creation of the heavenly bodies. It also accounts for the uniformity of the chemical composition of the entire universe, demonstrated by the spectroscope, as it gives a means, through the agency of such ether, of interchange between the heavenly bodies. One of the objects of an investigation into the elasticity or compressibility of gases under low pressure, undertaken by me in the seventies, was to trace, as far as the then existing methods of measuring low pressures permitted, the changes proceeding in gases under low pressures. The discrepancies from Boyle's law observed (by me and M. Kirpitchnikoff, 1874) for all gases, and subsequently confirmed by Ramsay and others (although still denied by some investigators), indicate a certain uniformity in the behaviour of all gases and a tendency in them towards a certain limiting expansion at low pressures, just as there is a limit to compression (liquefaction and the critical state). But determinations of very low pressures are accompanied by insurmountable difficulties. It proved practically impossible to measure, with any degree of accuracy, pressures under tenths of a millimetre of mercury, and this is far too large a figure for such rarefied media as are supposed to exist at an elevation of even 50 kilometres above the sea level. Hence the conception of the ether as a highly rarefied atmospheric gas cannot so far be subjected to experimental investigation and measurement, which alone can direct the mind in the right direction and lead to reliable results.

But, beyond this, the conception of the ether as a limiting state of expansion of vapours and gases cannot sustain even the most elementary analysis, for ether cannot be understood otherwise than as an all-pervading ubiquitous substance, and this is not the property of either gases or vapours. Both the latter are liquefiable under pressure, and cannot be said to permeate all substances, although they are widely distributed in nature, even in meteorites. Moreover—and this is most important—they vary infinitely in their chemical nature and in their relations to other substances, while the ether, as far as is known, is invariable. Owing to the variety of their chemical properties, all vapours and gases should react differently on the bodies which they permeate if they were components of the ether.

Before proceeding further, I think it necessary to justify the chemical views here and elsewhere brought into play. In the days of Galileo and Newton it was possible, although difficult, to conceive ether apart from them. But now it would be contrary to the most fundamental principles of natural science, for chemistry, since Lavoisier, Dalton, and Avogadro Gerhardt, has acquired the most sacred rights of citizenship in the great company of the natural sciences, and by placing the mass (weight) of a substance among its paramount conceptions it has followed the path indicated by Galileo and Newton. Moreover, chemistry and its methods alone have promoted in science a desire to apprehend bodies and their phenomena in their ultimate relations, through a conception of the reaction of their infinitely small parts or atoms, which may in fact be regarded as indivisible individuals, having nothing in common with the mechanically indivisible atoms of the ancient metaphysicians. There are many proofs of this; it will suffice to mention the fact that the atoms of modern science have often been explained by vortex rings; that there was formerly a strong inclination to conceive the chemical atoms as built up of themselves, or of a 'primary matter'; and that recently, especially in speaking of the radio-active substances, a division of chemical atoms into yet smaller 'electrons' begins to be recognised—all of which would be logically impossible were the atom regarded as mechanically indivisible. Chemically the atoms may be likened to the heavenly bodies, the stars, sun, planets, satellites, comets, &c. The building up of molecules from atoms, and of substances from molecules, is then conceived to resemble the building up of systems, such as the solar system, or that of twin stars or constellations, from these individual bodies. This is not a simple play of words in modern chemistry, nor a mere analogy, but a reality which directs the course of all chemical research, analysis, and synthesis. Chemistry has its own microscope for investigating invisible regions, and being an archi-real science it deals all the time with its invisible individualities without considering them mechanically indivisible. The atoms and molecules which are dealt with in all provinces of modern mechanics and physics cannot be other than the atoms and molecules defined by chemistry, for this is required by the unity of science. And therefore the metaphysicians of the present day should, for the advancement of knowledge, regard atoms in the same sense as that in which they are understood by natural science and not after the manner of the ancient metaphysicians of the Chinese or Greek school. If the Newtonian theory of gravity revealed the existence of forces acting at infinitely great distances, the chemistry of Lavoisier, Dalton, and Avogadro Gerhardt, on the other hand, disclosed the existence of forces of immense power acting at infinitely small distances, and transmutable into all other forms of energy, mechanical and physical. Thus all the present-day fundamental conceptions of natural science—and consequently the conception of the ether—must necessarily be considered under the combined influence of chemical, physical, and mechanical teachings. Although sceptical indifference is prone to discern only a 'working hypothesis' in the conception of the ether, yet the earnest investigator, seeking the reality of truth, and not the image of fantasy, is forced to ask himself what is the chemical nature of the ether.

Before endeavouring to give an answer respecting the chemical nature of ether, I think it necessary to state my opinion regarding the belief held by some in the unity of the substance of the chemical elements and their origin from one primary form of matter. According to this view, ether consists of this primary matter in an unassociated form, that is, not in the form of the elementary atoms or molecules of substances, but as the constituent principle out of which the chemical atoms are formed. This view has much that is attractive. The atoms are regarded as proceeding from primary matter in the same way as celestial bodies are sometimes represented as being formed from disunited bodies, such as cosmic dust, &c. The celestial bodies so formed remain surrounded by the cosmic dust, &c., from which they took their origin. So also the atoms remain in the midst of the all-pervading and primary ether from which they took their origin. Some persons assume also that atoms can be split up into their dust or primary matter, just as comets break up into falling stars; and that as the geological changes of the earth or the building up and association of heavenly bodies proceed before our eyes, so also do the atoms break up and form again in the silence of their eternal evolution. Others, without denying the possibility of such a process in exceptional, rare cases, consider the world of atoms to have been established once for all, and do not admit the possibility of decomposing the atom into its primary matter, or of forming new atoms of any chemical element from this primary matter by experimental means. In a word, they regard the process of the creation of atoms as finite and not subject to repetition, while they consider the ether as the residue remaining after the formation of atoms. This view need not be considered here, it being solely the fruit of imagination and unproved by any experimental investigation. But the former theory of a progressive evolution of the substance of atoms cannot be passed unnoticed by chemistry, for fundamental principles of this science are the indestructibility of matter and the immutability of the atoms forming the elements. If ether were producible from atoms and atoms could be built up from ether, the formation of new unlooked-for atoms and the disappearance of portions of the elements during experiment would be possible. A belief in such a possibility has long been held in the minds of many by force of superstition; and the more recent researches of Emmens to convert silver into gold, and those of Fittica (1900) to prove that phosphorus can be transformed into arsenic, show that it yet exists. In the fifty years during which I have carefully followed the records of chemistry, I have met with many such instances, but they have always proved unfounded. It is not my purpose here to defend the independent individuality of the chemical elements, but I am forced to refer to it in speaking of the ether, for it seems to me that, besides being chemically invalid, it is impossible to conceive of ether as a primary substance, because such a substance should have some mass or weight and also chemical relations—mass in order to explain the majority of phenomena proceeding at all distances up to the infinitely great, and chemical relations in order to explain those proceeding at distances infinitely small or commensurable with the atoms. If the question were restricted to the ether which fills space and serves as a medium for the transmission of energy, it would in a way be possible to limit oneself to the supposition of mass without reference to its chemical relations and even to consider the ether as a primary matter, just as the mass of a planet may be conceived without regarding its chemical composition. But such an indifferent, indefinite ether loses all sense of reality and awakens the misgivings of the earnest investigator, directly he realisès that it must permeate all substances. The necessity of an easy and perfect permeation of all bodies by the ether has to be admitted, not only for the comprehension of many physical phenomena (such as those of optics), but also owing to the great elasticity and rarity of the ethereal substance, the atoms of which are always conceived as being far more minute than the atoms and molecules of the known chemical substances. Moreover, this permeability of ether in all bodies explains why it cannot be isolated from substances, which indeed behave in respect to ether like a sieve to water or air. The capacity of the ether to penetrate all substances may, however, be regarded as the ideal of the diffusion of gases through metals and other diaphragms. Hydrogen, which has a small atomic weight and is the slightest of all known gases, not only diffuses more rapidly than any other gas, but also has the faculty of penetrating through walls of such metals as platinum and palladium, which are impervious to other gases. This property is certainly due, not only to the rapidity of the motion of the molecules of hydrogen, closely connected with its small density, but also to a chemical faculty of the same kind as is exhibited in the formation of metallic hydrides, of solutions, alloys, and other indefinite compounds. The mechanism of this penetration may be likened (at the surface of the body penetrated) to the solution of a gas in a liquid, that is, to the gaseous particles leaping into the interstices between the particles of the liquid with a retardation of their motion (a partial liquefaction of the gas), and a bringing into harmony of the motion of both kinds of particles. The condensed gas absorbed at the surface of contact travels in all directions through the body, and diffuses from one layer to another until it entirely permeates it. The possibility of gaseous hydrogen acting thus is evident from the fact that even gold diffuses through solid lead under the same force. At length, at the opposite surface of the body penetrated, the condensed gas will find it possible to escape into greater freedom, and will continue to pass in this direction until its degree of concentration becomes the same on both sides. When this takes place it does not set up a state of rest, but one of mobile equilibrium, that is, equal numbers of molecules or atoms will escape and leap in on the two sides. If, as it must, ether have the faculty of permeating all substances, it must be even lighter and more elastic (greater *vis viva*) than hydrogen, and, what is most important, must have a less capacity than hydrogen to form chemical compounds with the bodies it permeates. Compounds are characterised by the fact that the diverse atoms in them form systems or molecules, in which the different elements are in compatible, harmonious motion. We must therefore suppose that such a state of harmonious motion, of, for instance, hydrogen and palladium, is actually set up in those atoms of hydrogen which permeate the palladium, and that in so doing it forms with the palladium some compound (either Pd_2H or another) which easily dissociates when heated. Hence it seems to me that the atoms of ether are so void of this faculty of forming compounds (which is already weak in hydrogen) that such compounds dissociate at all temperatures, and that therefore nothing beyond a certain condensation among the atoms of substances can be looked for in the ether.

Eight years ago it would have been most arbitrary to deny the existence, in the substance or atoms of ether, of the faculty of forming any compounds with other chemical elements, for in those days all the known elements were, directly or indirectly, capable of entering into mutual combination. But in 1894 Lord Rayleigh and Professor Ramsay discovered argon, and defined it as the most inactive element; this was followed by the discovery of helium, the existence of which Lockyer had predicted by its spectrum as a solar element, and subsequently by the separation of neon, krypton, and xenon from air. None of these five new gases have yet given any definite compounds, although they clearly evince the faculty of solution, i.e., of forming indefinite, easily dissociated compounds. Thus we have now every right to say that the ether is unable to form any stable compounds with other chemical atoms, although it permeates all substances.

Hence *the ether may be said to be a gas, like helium or argon, incapable of chemical combination.* This definition of ether requires further consideration. The recognition of the ether as a gas signifies that it belongs to the category of the ordinary physical states of matter, gaseous, liquid, and solid. It does not require the recognition of a peculiar fourth state beyond the human understanding (Crookes). All mystical, spiritual ideas about ether disappear. In calling ether a gas, we understand a 'fluid' in the widest sense; an elastic fluid having no cohesion between its parts. Furthermore, if ether be a gas, it has weight; this is indisputable, unless the whole essence of natural science, from the days of Galileo, Newton, and Lavoisier, be discarded for its sake. But since ether possesses so great a penetrative power that it passes through every envelope, it is, of course, impossible to determine experimentally its mass in a given amount of other substances, or the weight of a given volume of ether. We ought, therefore, not to speak of the imponderability of ether, but only of the impossibility of weighing it.

The preceding remarks are in exact accordance with the generally accepted conception of ether. The only addition made is to ascribe to ether the properties of a gas, like argon and helium, utterly incapable of entering into true chemical combination. This point lies at the basis of our investigation into the chemical nature of ether, and includes the following two fundamental propositions: (1) that the ether is the lightest (in this respect ultimate) gas, and is endowed with a high penetrating power, which signifies that its particles have, relatively to other gases, small weight and extremely high velocity; and (2) that ether is a simple body (element) incapable of entering into combination or reaction with other elements or compounds, although capable of penetrating their substance, just as helium, argon, and their analogues are soluble in water and other liquids.

The argon group of gases and the periodic system of the elements have such a close bearing upon our further consideration of the chemical nature of ether that it behoves us to look at them more closely.

When in 1869 I first showed the periodic dependence of the properties of the elements upon their atomic weights, no element incapable of forming definite compounds was known, nor was the existence of such an element even suspected. Therefore the periodic system was arranged by me in groups, series, and periods, starting in group I. and series I., with hydrogen as the lightest and least dense of all the elements. It never occurred to me that hydrogen might be the starting-point of a system of elements. Guided by this system, I was able to predict both the existence of several unknown elements and also their physical and chemical properties in a free and combined state. These elements, gallium, scandium, and germanium, were subsequently discovered by Lecoq de Boisbaudran, Nilson, and Winkler respectively. I made these predictions by following what is known in mathematics as a method of interpolation, that is, by finding intermediate points by means of two extreme points whose relative position is known. The fact of my predictions having proved true confirmed the periodic system of the elements, which may now be considered as an absolute law. So long as the law remained unconfirmed, it was not possible to extrapolate (i.e., to determine points beyond the limits of the known) by its means; but now such a method may be followed, and I have ventured to do so in the following remarks on the ether, as an element lighter than hydrogen. My reason for doing this was determined by two considerations. In the first place, I think I have not many years for delay; and, in the second place, n recent years there has been much talk about the division of atoms into more minute electrons, and it seems to me that such ideas are not so much metaphysical as metachemical, proceeding from the absence of any definite notions upon the chemism of ether, and it is my desire to replace such vague ideas by a more real notion of the chemical nature of the ether. For until someone demonstrates either the actual transformation of ordinary matter into ether, or the reverse, or else the transformation of one element into another, I consider that any conception of the division of atoms is contrary to the scientific teaching of the present day; and that those phenomena in which a division of atoms is recognised would be better understood as a separation or emission of the generally recognised and all-permeating ether. In a word, it seems to me that the time has arrived to speak of the chemical nature of ether, all the more so since, so far as I know, no one has spoken at all definitely on this subject. When I applied the periodic law to the analogues of boron, aluminium, and silicon, I was thirty-three years younger than now, and I was perfectly confident that sooner or later my prediction would be fulfilled. Now I see less clearly and my confidence is not so great. Then I risked nothing, now I do. This required some courage, which I acquired when I saw the phenomena of radio-activity. I then saw that I must not delay, that perhaps my imperfect thoughts might lead someone to a surer path than that which was opened to my enfeebled vision.

First, I shall treat of the position of helium, argon, and their analogues in the periodic system; then of the position of ether in this system; and conclude with some remarks on the probable properties of ether according to the position it occupies in the periodic system.

When, in 1895, I first heard of argon and its great chemical inertness, I doubted the elementary nature of the gas, and thought it might be a polymeride of nitrogen, N_3, just as ozone, O_3, is a polymeride of oxygen, with the difference that, while ozone is formed from oxygen with the absorption of heat, argon might be regarded as nitrogen deprived of heat. In chemistry nitrogen was always regarded as the type of chemical inertness, i.e., of an element which enters into reaction with great difficulty, and if its atoms lost heat in becoming condensed by polymerisation from N_2 to N_3, it would form a still less active body; just as silica, which is formed from silicon and oxygen with the evolution of heat, is more inert than either of them separately. Berthelot subsequently published a similar view on the nature of argon, but I have now long discarded this, and consider argon to be an independent element, as Ramsay held it to be from the very beginning. Many reasons induced me to adopt this view, and chiefly the facts that (1) the density of argon is certainly much below 21, namely, about 19, that of H being 1, while the density of N_3 would be about 21, for the molecular weight of $N_3 = 14 \times 3 = 42$, and the density should be half this; (2) helium, discovered by Ramsay in 1895, has a density of about 2 referred to hydrogen, and exhibits the same chemical inactivity as argon, and in its case this inactivity can certainly not be due to a complexity of its molecule; (3) in their newly discovered neon, krypton, and xenon, Ramsay and Travers found a similar inactivity which, in these cases also, could not be explained by polymerisation; (4) the independent nature of the separate spectra of these gases and the invariability of these spectra under the influence of electric sparks proved that they belong to a family of elementary gases different from all other elements; and (5) the graduation and definite character of the physical properties in dependence upon the density and atomic weight further confirm the fact of their being simple bodies, whose individuality, in the absence of chemical reactions, can only be affirmed from the constancy of their physical features. An instance of this is seen in the boiling-points (at 760 mm.) or temperatures at which the vapour pressures equal the atmospheric pressure, and at which the liquid and gaseous phases are co-existent:

—	Helium	Neon	Argon	Krypton	Xenon
Atomic weight . .	4	19·9	38	81·8	128
Observed density . .	2	9·95	18·8	40·6	63·5
Observed boiling-point .	−262°	−239°	−187°	−152°	−100°

This recalls the halogen group:

—	Fluorine	Chlorine	Bromine	Iodine
Molecular weight	38	79·9	159·9	254
Vapour density	19	35·5	80	127
Boiling-point	−187°	−34°	+57·7°	+183·7°

In both cases the boiling-point clearly rises with the atomic or molecular weight. When the elementary nature of the argon analogues and their characteristic chemical inactivity were once proved, it became essential that they should take their place in the periodic system of the elements; not in any of the known groups, but in a special one of their own, for they exhibited new, hitherto unknown chemical properties, and the periodic system embraces in different groups those elements which are analogous in their fundamental chemical properties, although not in dependence upon these properties but upon their atomic weight, which apparently—previous to the discovery of the periodic law—stands in no direct relation to these properties. This was a critical test for the periodic law and the analogues of argon, but they both stood the test with perfect success; that is, the atomic weights, calculated from the observed densities, proved to be in perfect accordance with the periodic law.

Although I assume that the reader is acquainted with the periodic law, yet it may be well to mention that if the elements be arranged in the order of their atomic weights it will be found that similar variations in their chemical properties repeat themselves periodically, and that the order of the faculty of the elements to combine with other elements also corresponds with the order of their atomic weights. This is seen in the following simple example.

All the elements having an atomic weight of not less than 7 and not more than 35·5 fall into two series:

Li = 7·0	Be = 9·1	B = 11·0	C = 12·0	N = 14·0	O = 16	F = 19·0
Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine
Na = 23·0	Mg = 24·3	Al = 27·0	Si = 28·4	P = 31·0	S = 32·1	Cl = 35·5
Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Chlorine

Each pair of elements present a great similarity in their chief properties; this is especially marked in the higher saline oxides, which in the lower series are:

$$Na_2O,\ MgO,\ Al_2O_3,\ SiO_2,\ P_2O_5,\ SO_3,\ Cl_2O_7,$$

or

$$Na_2O,\ Mg_2O_2,\ Al_2O_3,\ Si_2O_4,\ P_2O_5,\ S_2O_6,\ Cl_2O_7.$$

Thus the atomic order of the elements exactly corresponds to the arithmetical order from 1 to 7. So that the groups of the analogous elements may be designated by the Roman ciphers I. to VII.; and when it is said that phosphorus belongs to group V., it signifies that it forms a higher saline oxide, P_2O_5. And if the analogues of argon do not form any compounds of any kind, it is evident that they cannot be included in any of the groups of the previously known elements, but should form a special zero group which at once expresses the fact of their chemical indifference. Moreover, their atomic weight should necessarily be less than those of group I.: Li, Na, K, Rd, and Cs, but greater than those of the halogens, F, Cl, Br, and I, and this *a priori* conclusion was subsequently confirmed by fact, thus:

Halogens	Argon analogues	Alkali metals
	He = 4·0	Li = 7·03
F = 19	Ne = 19·9	Na = 23·05
Cl = 35·5	Ar = 38	K = 39·1
Br = 79·95	Kr = 81·8	Rb = 85·4
I = 127	Xe = 128	Cs = 132·9

The five well-known alkali metals correspond to the newly discovered argon analogues, and the atomic weights of both exhibit the same common law of periodicity. But the halogens and alkali metals are the most chemically active among the elements, and are, moreover, of opposite chemical character, the first being particularly prone to react with metals and the others with metalloids, the former appearing at the anode and the latter at the cathode. They must therefore stand at the two extremes of the periodic system, as in the scheme on p. 518.

Although this arrangement best expresses the periodic law, the distribution of the elements according to groups and series in the table on page 519 is perhaps clearer.

—				Higher saline oxides	Groups	Large periods. Elements of even series				—
Distribution of the Elements in Periods				R_2O	I	K = 39·1	Rb = 85·4	Cs = 132·9	—	Rd = 224
				RO	II	Ca = 40·1	Sr = 87·6	Ba = 137·4	—	Th = 232
				R_2O_3	III	Sc = 44·1	Y = 89·0	La = 139	Yb = 173	U = 239
				RO_2	IV	Ti = 48·1	Zr = 90·6	Ce = 140	—	—
				R_2O_5	V	V = 51·4	Nb = 94·0	—	Ta = 183	—
				RO_3	VI	Cr = 52·1	Mo = 96·0	—	W = 184	—
				R_2O_7	VII	Mn = 55·0	? = 99·4	—	—	—
					VIII	Fe = 55·9	Ru = 101·7	—	Os = 191	—
						Co = 59	Rh = 103·0	—	Ir = 193	—
						Ni = 59	Pd = 106·5	—	Pt = 194·9	—
Gaseous hydrides	Higher saline oxides	Groups	Small periods. Typical elements							
	R_2O	I	H = 1·008	Li = 7·03	Na = 23·05	Cu = 63·6	Ag = 107·9	—	Au = 197·2	—
	RO	II		Be = 9·1	Mg = 24·3	Zn = 65·4	Cd = 112·4	—	Hg = 200·0	—
	R_2O_3	III		B = 11·0	Al = 27·0	Ga = 70·0	In = 114·0	—	Tl = 204·1	—
RH_4	RO_2	IV		C = 12·0	Si = 28·4	Ge = 72·3	Sn = 119·0	—	Pb = 206·9	—
RH_3	R_2O_5	V		N = 14·04	P = 31·0	As = 75·0	Sb = 120·0	—	Bi = 208	—
RH_2	RO_3	VI		O = 16·00	S = 32·06	Se = 79	Te = 127	—	—	—
RH	R_2O_7	VII		F = 19·0	Cl = 35·45	Br = 79·95	I = 127	—	—	—
R	R	0	He = 4·0	Ne = 19·9	Ar = 38	Kr = 81·8	Xe = 128	—	—	—
						Elements of uneven series				

Series	Zero Group	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII			
0	*x*											
1	*y*	Hydrogen H=1·008										
2	Helium He=4·0	Lithium Li=7·03	Beryllium Be=9·1	Boron B=11·0	Carbon C=12·0	Nitrogen N=14·04	Oxygen O=16·00	Fluorine F=19·0				
3	Neon Ne=19·9	Sodium Na=23·05	Magnesium Mg=24·1	Aluminium Al=27·0	Silicon Si=28·4	Phosphorus P=31·0	Sulphur S=32·06	Chlorine Cl=35·45				
4	Argon Ar=38	Potassium K=39·1	Calcium Ca=40·1	Scandium Sc=44·1	Titanium Ti=48·1	Vanadium V=51·4	Chromium Cr=52·1	Manganese Mn=55·0	Iron Fe=55·9	Cobalt Co=59	Nickel Ni=59	(Cu)
5		Copper Cu=63·6	Zinc Zn=65·4	Gallium Ga=70·0	Germanium Ge=72·3	Arsenic As=75·0	Selenium Se=79	Bromine Br=79·95				
6	Krypton Kr=81·8	Rubidium Rb=85·4	Strontium Sr=87·6	Yttrium Y=89·0	Zirconium Zr=90·6	Niobium Nb=94·0	Molybdenum Mo=96·0	—	Ruthenium Ru=101·7	Rhodium Rh=103·0	Palladium Pd=106·5	(Ag)
7		Silver Ag=107·9	Cadmium Cd=112·4	Indium In=114·0	Tin Sn=119·0	Antimony Sb=120·0	Tellurium Te=127	Iodine I=127				
8	Xenon Xe=128	Cæsium Cs=132·9	Barium Ba=137·4	Lanthanum La=139	Cerium Ce=140	—	—		—	—	—	(—)
9		—	—		—	—	—	—				
10	—	—	—	Ytterbium Yb=173	—	Tantalum Ta=183	Tungsten W=184	—	Osmium Os=191	Iridium Ir=193	Platinum Pt=194·9	(Au)
11		Gold Au=197·2	Mercury Hg=200·0	Thallium Tl=204·1	Lead Pb=206·9	Bismuth Bi=208	—	—				
12	—	—	Radium Rd=224	—	Thorium Th=232	—	Uranium U=239					

Here x and y stand for two unknown elements having atomic weights less than that of hydrogen, whose discovery I now look for.

A reference to the above remarks on the argon group of elements shows first of all that such a zero group as they correspond to could not possibly have been foreseen under the conditions of chemical knowledge at the time of the discovery of the periodic law in 1869; and, although I had a vague notion that hydrogen might be preceded by some elements of less atomic weights, I dared not put forward such a proposal, because it was purely conjectural, and I feared to injure the first impression of the periodic law by its introduction. Moreover, in those days the question of the ether did not awaken much interest, for electrical phenomena were not then ascribed to its agency, and it is this that now gives such importance to the ether. But at the present time, when there can be no doubt that the hydrogen group is preceded by the zero group composed of elements of less atomic weights, it seems to me impossible to deny the existence of elements lighter than hydrogen.

Let us first consider the element in the first series of the zero group. It is designated by y. It will evidently exhibit all the fundamental properties of the argon gases. But first we must have an approximate idea of its atomic weight. To do this, let us consider the ratio of the atomic weights of two elements belonging to the same group of neighbouring series. Starting with Ce = 140 and Sn = 119 (here the ratio is 1·18), this ratio, in passing to the lower groups and series, increases constantly and fairly uniformly as the atomic weights of the elements under comparison decrease. But we shall limit our calculation to the first and second series, starting with Cl = 35·45; for (1) we are exclusively concerned with the lightest elements, (2) the ratio of the atomic weights is more accurate for these elements, and (3) the small periods of the typical elements (which should include the elements lighter than hydrogen) terminate with chlorine. As the atomic weight of chlorine is 35·45. and that of fluorine 19·0, the ratio Cl : F = 35·4 : 19·0 = 1·86; so also we find:

Group VII	Cl : F	= 1·86
VI	S : O	= 2·00
V	P : N	= 2·21
IV	Si : C	= 2·37
III	Al : B	= 2·45
II	Mg : Be	= 2·67
I	Na : Li	= 3·28
0	Ne : He	= 4·98

This proves that the ratio in the given series distinctly and progressively increases in passing from the higher to the lower groups; and, moreover, that it varies most rapidly between the first and zero groups. It follows therefore that the ratio He : y will be considerably greater than the ratio Li : H, which is 6·97, so that the ratio He : y will be at least 10 and probably even greater. Hence, as the atomic weight He = 4·0, the atomic weight of y will be not greater than $\frac{4\cdot0}{10} = 0\cdot4$ and probably less. Such an analogue of helium may perhaps be found in coronium, whose spectrum, clearly visible in the solar corona above (that is, further from the sun than) that of hydrogen, is simple like that of helium, which seems to indicate that it belongs to a gas resembling helium, which was also predicted from its spectrum by Lockyer. Young and Harkness independently observed the spectrum of this unknown element during the solar eclipse of 1869. It is characterised by a bright-green line of wave-length 531·7$\mu\mu$, while helium is characterised by a yellow line, 587$\mu\mu$. Nasini, Anderlini, and Salvadori think that they discovered traces of coronium in their observations on the spectra of volcanic gases (1893). And as the lines of coronium were also observed, even at distances many times the radius of the sun above its atmosphere and protuberances, where the hydrogen lines are no longer visible, it is evident that coronium should have a less density and atomic weight than hydrogen. Moreover, as the ratio of the specific heats (at a constant pressure and for a constant volume) of helium, argon, and their analogues gives reason for thinking that their molecules (i.e., the amount of matter occupying, according to Avogadro-Gerhardt's law, a volume equal to the volume of two parts by weight of hydrogen) contain only one atom (like mercury, cadmium, and most metals), it follows that, if 0·4 be the greatest atomic weight of the element y, its density referred to hydrogen should be less than 0·2. Consequently the molecules of this gas will, according to the kinetic theory of gases, move 2·24 times faster than those of hydrogen, and if, as Stoney (1894–1898) and Rostovsky (1899) endeavour to prove, the progressive motion of the molecules of hydrogen and helium be such that they can leap out of the sphere of the earth's attraction, then a gas whose density is at least five times less than that of hydrogen could certainly only exist in the atmosphere of a body having as great a mass as the sun.

However, this y—coronium or some other gas with a density about 0·2—cannot possibly be ether, its density being too great. It wanders, perhaps for ages, in the regions of space, breaks from the shackles of the earth, and again comes within its sphere, but still it cannot escape from the regions of the sun's attraction, and there are many heavenly bodies of greater mass than the sun. But the atoms of ether must be of another kind; they must be capable of overcoming even the sun's attraction, of freely permeating all space, and of penetrating everything and everywhere. The element y, however, is necessary for us to be able to mentally realise the lightest and therefore swiftest element x, which I consider may be looked upon as the ether.

We have seen that, besides the ordinary groups of the chemically active elements, a zero group of chemically inactive elements must now be recognised for helium, argon, and their analogues. Thanks to Ramsay's exemplary researches, these elements are now tangible realities, authentic gases foreign to chemical association, that is, distinguished by their specific property of not being chemically attracted to each other or to other atoms even at infinitely small distances, and yet having weight, that is, subject to the laws of attraction of mechanics, which has nothing in common with chemical attraction. There is some hope that gravity may in some way or another be explained by means of pressure or impact acting from all sides, but chemical attraction, which only acts at infinitely small distances, will long remain an incomprehensible problem. The problem of the ether is more or less closely connected with that of gravity, and gains in simplicity when all question of the chemical attraction of the atoms of ether is excluded, and this is accomplished by placing it in the zero group. But if the series of the elements begins with series I containing hydrogen, the zero group has no place for an element lighter than y, like ether. I therefore add a zero series, besides a zero group, to the periodic system, and place the element x in this zero series, regarding it (1) as the lightest of all the elements both in density and atomic weight; (2) as the most mobile gas; (3) as the element least prone to enter into combination with other atoms; and (4) as an all-permeating and penetrating substance. Of course, this is an hypothesis, but it is one constructed not for purely 'working' ends, but simply from a desire to extend the real periodic system of the known elements to the confines or limits of the lowest dimensions of atoms, which I cannot and will not regard in the light of a simple nullity called mass.

Being unable to conceive the formation of the known elements from hydrogen, I can neither regard them as being formed from the element x, although it is the lightest of all the elements. I cannot admit this, not only because no fact points to the possibility of the transformation of one element into another, but chiefly because I do not see that such an admission would in any way facilitate or simplify our understanding of the substances and phenomena of nature. And when I am told that the doctrine of unity in the material of which the elements are built up responds to an aspiration for unity in all things, I can only reply that at the root of all things a distinction must be made between matter, force, and mind; that it is simpler to admit the germs of individuality in the material elements than elsewhere; and that no general relation is possible between things unless they have some individual character resident in them. In a word, I see no object in following the doctrine of the unity of matter, while I clearly see the necessity of recognising the unity of the substance of the ether and of realising a conception of it, as the uttermost limit of that process by which all the other atoms of the elements were formed, and by which all substances were formed from these atoms. To me this kind of unity is far more real than any conception of the formation of the elements from a single primary matter. Neither gravity nor any of the problems of energy can be rightly understood without a real conception of the ether as a universal medium transmitting energy at a distance. Moreover, a real conception of ether cannot be obtained without recognising its chemical nature as an elementary substance, and in these days no elementary substance is conceivable which is not subject to the periodic law.

I shall therefore, in conclusion, endeavour to show what consequences should follow from the above conception of the ether, from an experimental or realistic point of view, even should it never be possible to isolate or combine or in any way grasp this substance.

Although it was possible to approximately determine the atomic weight of the element y on the basis of that of helium, this cannot be repeated for the element x, because it lies at the frontier or limit, about the zero point of the atomic weights. Moreover, the analogues of helium cannot serve as a basis owing to the uncertainty of their numerical data. However, if the ratio of the atomic weights be Xe : Kr = 1·56 : 1; Kr : Ar = 2·15 : 1; and Ar : He = 9·5 : 1, we find that He : x = 23·6 : 1; or if He = 4·0, that the atomic weight of $x = 0{\cdot}17$. This must be considered the maximum possible value. Most probably the atomic weight of x is far less, for the following reasons. If the gas in question be an analogue of helium, its molecule will contain one atom, and therefore its density, referred to that of hydrogen, must be about half its atomic weight or $\frac{x}{2}$, where x is the atomic weight. In order to be able to permeate throughout all space, its density must be so small, compared with that of hydrogen, that its molecular motion would allow it to overcome the attraction, not only of the earth and sun, but also of all the stars, as otherwise it would accumulate about the largest mass and not fill all space. The velocity of the molecular motion of a gas by which the gaseous pressure is determined—by the number of impinging particles and their *vis viva*—is calculated, according to the kinetic theory of gases, by an expression containing a constant divided by the square root of the density of the gas and multiplied by the square root of $(1 + at)$ which expresses the expansion of the gas by heat. In the case of hydrogen (density = 1) at $t = 0°$, the mean velocity of the particles, calculated on the basis that a litre of hydrogen at 0° and 760 mm. weighs about 0·09 grm., is 1843 metres a second, that of oxygen being 461 metres, for its density is 16 times that of hydrogen, i.e., $v = \frac{1843}{4} = 461$. Thus the velocity increases as the density becomes less and as the temperature becomes greater, but does not depend upon the number of molecules in a given volume; and if our gas have an atomic weight x and density (referred to hydrogen) $\frac{x}{2}$, then the velocity of its molecules will be:

$$v = 1843\sqrt{\frac{2(1 + at)}{x}} \quad . \quad . \quad . \quad . \quad . \quad \text{(I)}$$

In this expression x is the unknown quantity, to find which we must know t and v, or the velocity required by the particles to escape from the sphere of the earth's, sun's, and stars' attraction, like the projectile in Jules Verne's 'Voyage to the Moon.'

As regards the temperature of space, this can only be regarded as the absolute zero by those who deny the material nature of the ether, for temperature in a perfect vacuum or in space devoid of matter is an absurdity, and a solid such as an aërolite or thermometer introduced into such space would alter the temperature, not by contact with the surrounding medium, but solely by radiation. But if space be filled with the substance of ether, it not only may, but must have its own temperature, which evidently cannot be absolute zero. Many methods have been tried to determine this temperature, but it is unnecessary to discuss them here. Suffice it to say that no one has found it less than −150° or above −40°; as a rule, the limits are taken as −100° and −60°. It is hopeless to expect any definite or exact data on this subject, and probably the temperature varies in different localities owing to radiation being different in different parts of space. Moreover, the value of t between $-100°$ and $-60°$ has hardly any significance in an approximate evaluation of x, as only the maximum value of x can be calculated by the expression (I); for there can be no question of any exact value, all that is required being to obtain an idea of the order in which x stands among the elements. We therefore take the mean temperature $t = -80°$; then if $a = 0{\cdot}000367$,

$$v = \frac{2191}{\sqrt{x}} \quad \text{or} \quad \frac{4800000}{v^2} \quad . \quad . \quad . \quad . \quad \text{(II)}$$

where x is the atomic weight of the gaseous element required referred to hydrogen, and v the velocity of motion of its particles at $-80°$ in metres per second.

This velocity must now be determined. We know that a body thrown up in the air falls back to the earth, and in so doing describes a parabola. The height of its flight increases as its initial velocity is made greater, and it is evident that this velocity might be such that the body would pass beyond the sphere of the earth's attraction, and fall on some other heavenly body, or rotate about the earth as a satellite by virtue of the laws of gravitation. It has been calculated that to do this the velocity of the body must exceed the square root of double the mass of the attracting body divided by the distance from its centre of gravity to the point at which the velocity is to be determined. The mass of the earth is calculated in absolute units from the mean radius of the earth ($= 6{,}373{,}000$ metres) and the mean attraction of gravity at the surface of the earth ($= 9{\cdot}807$ metres), for the attraction of gravity is equal to the mass divided by the square of the distance (in this instance, the square of the earth's radius), and therefore the mass of the earth $= 398.10^{12}$, and the velocity sought for must therefore exceed 11,190 metres a second. Hence, according to formula (II), the atomic weight of such a gas must be less than 0·038 to enable it to escape freely from the earth's atmosphere into space. All gases of greater atomic weight, not only hydrogen and helium, but even the gas y (coronium ?), will remain in the earth's atmosphere.

The mass of the sun is approximately 325,000, if that of the earth be taken as unity. Hence the absolute magnitude of the sun's mass will be nearly 129.10^{18}. The radius of the sun is 109·5 times greater than that of the earth, i.e., nearly 698.10^{6} metres. Hence only bodies or particles having a velocity of not less than $\sqrt{\frac{2.129.10^{18}}{698.10^{6}}}$ or about 608,300 metres a second, could escape from the surface of the sun. According to formula (II), the atomic weight of a gas x having such a velocity will not be greater than 0·000013, and its density will be half this figure. Hence the atomic weight and density of such a gas, which, like the ether, permeates space, must at all events be less than this figure. This is inevitable because there are stars of greater mass than the sun. This has been proved by researches made on the double stars.

The most exact data we now possess concern Sirius, whose total mass (including that of its satellites) is 3·24 times that of the sun. To determine this it was necessary to investigate not only the relative motion of both stars, but also the parallax of this system. In the case of Sirius it was possible to determine the ratio of the masses of the two stars. This was found to be 2·05; so that the mass of one star is 2·20, and that of the other 1·04, times that of the sun. In the following cases only the total mass of the two twin stars was determined relative to that of the sun:

α Centauri	2·0
70 Ophiuchi	1·6
μ Cassiopeiæ	0·52
61 Cygni	0·34
γ Leonis	5·8
γ Virginis	32·70

The mass of β Persei with its satellites is 0·67 time that of the sun, that of the star being twice that of its satellite. The triple star 40 Eridium has a mass 1·1 time that of the sun, the mass of the brightest star being 2·37 times that of the other two.

It appears, therefore, that although there are some stars which are greater, and some which are less, still the mass of the sun is nearly the average of that of the other stars. For our purpose we need only consider the stars of much greater mass than the sun. That of the double star γ Virginis has a common mass about 33 times that of the sun. There is no reason for thinking that this is the maximum, and it will therefore be safer to infer that there may be stars whose mass exceeds 50 times that of the sun; but I do not think it likely that a larger mass than this is in the nature of things. To complete our calculation it is also necessary to know the radius of the stars, about which we have no direct data. However, the composition and temperature of the stars may give a clue. Spectrum analysis proves that the terrestrial chemical elements occur in the most distant heavenly bodies, and from analogy there seems no doubt that the general mass composition of these bodies is very similar in all cases; that is to say, they are composed of a dense core surrounded by a less dense crust and an atmosphere which becomes gradually rarefied. Thus the composition of the stars probably differs but little from that of the sun, and the density is determined by the composition, temperature, and pressure. Only at the core can the density differ much from that of the sun, but this cannot greatly affect the average density. Neither can the temperature of the stars differ greatly from that of the sun. Moreover, a rise of temperature would tend to increase the diameter of the star, and this would decrease the value of the velocity required by the gaseous particles to escape from the sphere of attraction. It appears, therefore, that for the purposes of our calculation the average density of the large stars may be taken as nearly that of the sun, and therefore that the radius of a star whose mass is n times that of the sun will be $\sqrt[3]{n}$ times the radius of the sun. We now have all the data necessary for calculating the velocity required by gaseous particles to escape from the sphere of attraction of a star 50 times greater than the sun.

Its mass is $50.129.10^{18}$, or nearly 65.10^{20}, and its radius nearly $698.10^{6}.\sqrt[3]{50}$, or 26.10^{8}. Hence the velocity required will be nearly:

$\sqrt{\frac{2.65 \times 10^{20}}{26 \times 10^{8}}}$ = 2,240,000 metres per second, or 2,240 kilometres per second.

The great magnitude of this velocity, v, and its proximity to that of light (300,000,000 metres a second) provoke the following inquiry: How much must the mass of a heavenly body exceed that of the sun in order to retain on its surface particles endowed with a velocity of 3.10^{8} metres per second, if its mean density were equal to that of the sun? This may be calculated from the fact that if the mean density of the two luminaries be equal, the velocities of bodies able to escape into space from the spheres of attraction will stand in the ratio of the cube roots of their masses, and therefore a luminary from whose surface particles endowed with a velocity of 300,000,000 metres per second could escape must have a mass 120,000,000 times that of the sun, for only particles having a velocity of 608,000 metres a second can escape from the sun, and this stands to 300,000,000 in the ratio 1 : 493, and the cube of 493 is nearly 120,000,000.

But, so far we have no reason for admitting the existence of such a huge body, and therefore it seems to me that the velocity of the particles of our gas (ether) must, in order to permeate space, be greater than 2,240,000 metres a second, and probably less than 300,000,000 metres a second.

Hence the atomic weight of x as the lightest elementary gas, permeating space and performing the part of the ether, must be within the limits (formula II) of 0·000,000,96 and 0·000,000,000,053, if that of H = 1.

I think it is impossible, under the present conditions of our scientific knowledge, to admit the latter value, because it would in some measure answer to a revival of the emission theory of light, and I consider that the majority of phenomena are sufficiently explained by the fact that *the particles and atoms of the lightest element* x, *capable of moving freely everywhere throughout the universe, have an atomic weight nearly one millionth that of hydrogen, and travel with a velocity of about* 2,250 *kilometres per second.*

When I was making these calculations my friend Professor Dewar sent me his presidential address to the Belfast meeting of the British Association. In it he expresses the thought that the highest regions of the atmosphere, which are the seat of the aurora borealis, must be considered to be the province of hydrogen and of the argon analogues. This is only a few steps from the yet more distant regions of space, and from the necessity of recognising the existence of a still lighter gas capable of permeating and filling space, and thus giving a tangible reality to the conception of the ether.

In conceiving of the ether as a gas endowed with the above properties and belonging to the zero group of elements, I desired before all to extract from the periodic law that which it was able to give and to tangibly explain the materiality and universal presence of an ethereal substance throughout nature, and also to explain its faculty of permeating all substances, gaseous, liquid, and solid. The atoms of even the lighter elements forming the ordinary substances being several million times heavier than those of ether, they are not likely to be greatly influenced in their mutual relations by its presence.

Of course there are still many problems to be solved, but I think the majority are unfathomable, and I have no intention of raising them here or of trying to solve those which appear capable of being solved. My only purpose has been to state my opinion on a subject about which I know many are thinking and some are beginning to speak.

Without going into a further development of our subject, I should like to acquaint the reader with some, at first sight, auxiliary circumstances which guided my thoughts and led me to publish my opinions. These consist of a series of recently discovered physico-chemical phenomena which are not subject to the ordinary doctrines of science, and have caused many to return to the emission theory of light, or to accept the, to me, vague hypothesis of electrons, without trying to explain to the utmost the familiar conception of an ethereal medium transmitting luminous vibrations, &c. This more especially refers to radio-active phenomena.

I need not describe these most remarkable phenomena, assuming that the reader is more or less acquainted with them, and shall only mention that a perusal of the literature of the subject, and what I saw in M. Becquerel's laboratory and heard from him and M. and Madame Curie, gave me the impression of some peculiar state proper chiefly (but not exclusively, just as magnetism is chiefly, but not exclusively, the property of iron and cobalt) to uranium and the thorium compounds.

As uranium and thorium, and also radium, judging from Madame Curie's researches (1902), have the highest atomic weights (U = 239, Th = 232, and Rd = 224) among the elements, they may be looked upon as suns, endowed with the highest degree of that individualised attractive capacity, a mean between gravity and chemical affinity, which is seen in the absorption of gases, solution, &c. By conceiving the substance of the ether as the lightest of gases, x, deprived, like helium and argon, of the power to form stable definite compounds, it need not be imagined that this gas is deprived of the faculty of, as it were, dissolving in or accumulating about large centres of attraction like the sun among heavenly bodies, or uranium and thorium in the world of atoms. As a matter of fact, direct experiment proves that helium and argon are able to dissolve in liquids, and, moreover, to individualise this faculty according to either their own nature or that of the liquid and according to the temperature. If the ether is a gas, x, it must naturally accumulate from all parts of the universe towards the medium or mass of the sun, just as the gases of the atmosphere accumulate in a drop of water. And the lightest of gases, x, will also accumulate about the heaviest atoms of uranium and thorium, and perhaps change its form of motion like a gas dissolved in a liquid. This will not be a definite act of combination, determined by a conformable harmonious motion, like the motion of a planet and its satellites, but an embryo of such a motion, resembling that of a comet in the region of heavenly individualisations, and it may be looked for sooner in the region of the heaviest atoms of uranium and thorium than in those of the lighter elements, just as a comet falling from space into the planetary system revolves round the sun and then once more escapes into space. If such a special accumulation of ether atoms about the molecules of uranium and thorium be admissible, they might be expected to exhibit peculiar phenomena, determined by the emission of a portion of this ether held by particles of normal mean velocity and by new ether entering into the sphere of attraction. It seems to me that the optical and photo-radiant phenomena, not to mention the loss of electrical charges, indicate a material flow of something which has not been weighed, and it appears to me that they might be understood in this manner, for peculiar forms of the entrance and egress of ether atoms should be accompanied by such disturbances in the ethereal medium as give the phenomena of light. M. and Madame Curie showed me the following experiment, for instance. Two small flasks were connected together by a lateral tube fused into their necks, and having a stopcock in the middle. The cock being closed, a solution of the radio-active substance was poured into one of the flasks, while a gelatinous white precipitate of sulphide of zinc, shaken up in water, was placed in the other flask. Then both flasks were closed. So long as the cock between the flasks remains closed, nothing is visible in the dark; but directly it is opened, the sulphide of zinc becomes brilliantly fluorescent and continues so as long as the tube connecting the flasks remains open. This experiment gives the impression of an emissive flow of something material from the radio-active substance, and, in a sense, seems comprehensible if we assume that a peculiar rarefied ether gas, capable of exciting luminous vibrations, enters and passes off from the radio-active substance. Just as any kind of motion may be set up in a gas, not only by a solid piston, but also by the motion of another portion of the same gas, so also the phenomenon of light, i.e., a certain transverse vibration of ether, may be produced not only by the molecular motion of particles of other bodies (by heating them or otherwise) bringing the ether from its state of mobile equilibrium, but also by a certain change in the motion of the ether atoms themselves; i.e., by their destroying their own equilibrium which may be caused in the case of the radio-active bodies by the massiveness of the atoms of uranium and thorium, just as the luminosity of the sun may be, I think, due to its great mass being able to accumulate ether in far larger quantities than the planets, &c. I think that the radio-luminous phenomena, i.e., such as proceed at right angles to the ray of the vibration of the ether medium, consisting of minute atoms in rapid motion, are, as a matter of fact, more complex than has hitherto been thought, chiefly owing to the fact that the velocity of the ether atoms is not very much less (130 times) than that of the propagation of their transverse vibrations. This at all events was the impression I acquired from the radio-active phenomena I saw, and I do not conceal it, although I consider it very difficult to form any opinion on this still dim province of the phenomena of light.

In conclusion, I may mention another class of phenomena, which led me to this conception of the ether. Dewar, about 1894, in his researches on the phenomena proceeding at low temperatures, observed that the phosphorescence of many substances, and especially of paraffin, becomes more intense at the temperature of liquid air (between −181° and −193°). Now, it appears to me that this is due to the fact that paraffin and such like substances have a great capacity for condensing the atoms of ether at very low temperatures. In other words that the solubility (absorption) of the ether in some bodies increases in extreme cold. They therefore become more phosphorescent, for the vibrations of light are then set up in the phosphorescent substances, not only by their own atoms (having the property of illumination at their surface, of passing into a state of peculiar tension, which causes, when the act of illumination ceases, the ether to vibrate), but also by the atoms of ether which condense in these bodies and set up a rapid state of interchange with the surrounding medium.

It seems to me that this conception of ether, as a peculiar all-permeating gas, gives a means, if not of analysing such phenomena, at all events of understanding their possibility. I do not regard my imperfect endeavour to explain the nature of ether from a chemical point of view as more than the expression of a series of thoughts which have arisen in my mind, and which I have given vent to solely from a desire that these thoughts, being suggested by facts, should not be utterly lost. Most probably similar thoughts have come to many, but unless they are enunciated they often pass away without being further developed. If they contain a particle of that natural truth which we all seek, my effort will not have been in vain; it may then be worked out, embodied, and corrected, and if my conception be proved false in its basis, it will prevent others from repeating it. I know of no other way for slow and steady progress. And even if it be found impossible to recognise in the ether the properties of the lightest, most mobile, and chemically inactive gas, still, if we keep to the realism of science, we cannot deny its substantiality, and this requires a search for its chemical nature. My effort is no more than a tentative answer to this primary question, and its one object is to bring this question to the fore.

October 1902.

INDEX OF AUTHORITIES

INDEX OF SUBJECTS

PRINTED BY
SPOTTISWOODE AND CO. LTD., NEW-STREET SQUARE
LONDON